

Fate and Transport of Plutonium and Americium in the Subsurface of OU 7-13/14

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June 2003*



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ABSTRACT

Plutonium and americium have been released into the environment as a result of nuclear weapons testing and energy production. A large portion of plutonium and americium is currently stored in waste deposits, some of which have leaked and released actinides into the subsurface. Migration of actinides through the subsurface is generally limited because of their low-aqueous solubility and strong sorption to minerals and organic materials. However, in a few locations, a fraction of plutonium and americium moved considerable distances through the subsurface. The purpose of this manuscript is to review literature on plutonium and americium in the subsurface and to develop a conceptual model for plutonium and americium fate and transport in the subsurface. First, the occurrence and distribution of plutonium and americium in the terrestrial environment is summarized. This shows that, worldwide, most atmospherically deposited plutonium and americium is concentrated in the top few centimeters of soil, but a fraction of actinides has moved considerably farther distances. The environmental chemistry of plutonium and americium is discussed, and the major chemical reactions relevant for environmental conditions are presented, including redox, hydrolysis, complexation, polymerization, and sorption reactions. The geochemical reactions are then put into perspective with respect to transport mechanisms, which shows that colloid-facilitated transport is an important transport process for plutonium and americium. Colloid-facilitated transport of plutonium and americium can occur by way of inorganic, organic, or intrinsic colloids and will enhance movement of actinides through the subsurface. Total mass transported, however, will be limited by the amount of colloids present. A conceptual model for plutonium and americium fate and transport in the subsurface is presented. From this conceptual model, key issues are identified that must be resolved in order to understand and potentially quantify plutonium and americium fate and transport at the Idaho National Engineering and Environmental Laboratory site in Idaho Falls, Idaho.

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1. INTRODUCTION

Plutonium has been released into the environment by human activities related to weapons testing and energy production. Both nonpoint-source and point-source pollution with plutonium has occurred. Nonpoint-source pollution originated mainly from atmospheric nuclear bomb tests between 1945 and 1962 and from a satellite accident in 1964 (Hardy, Krey, and Volchok 1973). Point-source pollution has been caused by accidents, such as the nuclear-weapons-carrying airplanes that crashed in Spain in 1966 and Greenland in 1968, by release of plutonium from production facilities and waste disposal operations, and by underground nuclear bomb testing. No matter the environmental compartment in which plutonium was released, the radionuclide tends to accumulate in soil, sediment, and rocks. It has been found that plutonium sorbs very strongly to subsurface materials, and migration of plutonium through the subsurface is minimal. Past environmental monitoring has repeatedly shown that atmospheric plutonium fallout is concentrated in the first few centimeters of soil, demonstrating limited mobility of plutonium in the subsurface (Harley 1980; UNIPUB 1982 [Yamamoto, Komurs, and Sakanoue]; Bunzl et al. 1995).

Past monitoring studies were not designed to find the leading edge of plutonium distribution in soil but to pinpoint the location of the bulk of plutonium. Maximum transport distances of plutonium are difficult to infer from these studies. More recent evidence has indicated that, under certain conditions, plutonium can be mobile in the subsurface. Enhanced mobility of plutonium has been postulated to occur under conditions of preferential flow (Bundt et al. 2000), colloidal transport (Kersting et al. 1999), or a combination of the two phenomena (Litaor, Barth, and Zika 1996; Litaor et al. 1998). These processes would allow plutonium to migrate much farther through the subsurface than expected based on chromatographic considerations commonly made for subsurface transport. Enhanced mobility of plutonium in the subsurface is of utmost concern for waste disposal and risk assessment and, if proven to be relevant, must be considered in fate and transport models.

The environmental chemistry of plutonium is complex. Plutonium has four oxidation states: Pu(III), Pu(IV), Pu(V), and Pu(VI). Each of these oxidation states has different sorption properties. Further, plutonium is a difficult element to work with experimentally. Standard chemical laboratories are usually not equipped with analytical tools to measure plutonium, and preserving the original oxidation state of plutonium in environmental samples is often difficult. Consequently, environmental fate and transport of plutonium are not as easily studied as other contaminants with laboratory experiments.

Americium-241 is a decay product of Pu-241 by β decay with a half-life of 14.4 years. Consequently, distribution of Am-241 in the environment follows closely that of Pu-241. Like plutonium, americium shows a bimodal mobility in the environment. Most americium accumulates in the top few centimeters of soil. Like plutonium, enhanced mobility of americium has been observed for a small fraction of americium attributed to a colloidal transport pathway (Kim 1986; Nagasaki, Tanaka, and Suzuki 1997b). Unlike plutonium, however, americium only occurs in one stable oxidation state (Am[III]) in the environment, and the geochemical behavior is substantially simpler than that of plutonium.

The objective of this manuscript is to develop a conceptual model for fate and transport of plutonium and americium in the subsurface and to outline how this model would be parameterized for implementation into fate and transport codes. The conceptual model is based on a review of pertinent literature on plutonium and americium fate and transport in the subsurface and provides an overview of environmental chemistry and hydrology of the two radionuclides.

2. INFORMATION SOURCES

Most information compiled and reviewed in this manuscript is taken from peer-reviewed technical publications. Research activities related to plutonium and americium fate and transport are currently ongoing in many laboratories, and preliminary results have been presented in conference abstracts. Such abstracts have been used when appropriate and available. A large body of pertinent literature about plutonium and americium exists in the form of internal reports from DOE national laboratories, such as Los Alamos and Argonne, or federal agencies, like the DOE or USGS. An effort has been made to obtain such reports, and the information has been incorporated in this review whenever possible.

Several reviews and summaries exist on environmental distribution of plutonium and americium (Hardy, Krey, and Volchok 1973; Harley 1980; Watters, Hakonson, and Lane 1983; Coughtrey et al. 1984, Vol. 4, pp. 1–462; Coughtrey et al. 1984, Vol. 5, pp. 1–235; Kudo 2001 [Taylor]), the geochemistry of plutonium and americium (Cleveland 1979; Choppin 1983; Carnall 1983; Kim 1986; Lieser 1995; Runde 2000; Kudo 2001 [Choppin and Morgenstern]; Zhang and Brady 2002 [Runde]), migration of radionuclides in subsurface media (Choppin 1992; Kudo 2001 [Choppin and Morgenstern]), and the role of colloid-facilitated transport of radionuclides (Zhang and Brady 2002 [Honeyman and Ranville]). Here, previous reviews on environmental (subsurface) distribution of the two actinides are updated with emphasis on the leading edge of concentration distributions, and environmental chemistry of actinides is discussed with respect to its relevance to transport in subsurface media. Transport behavior of plutonium and americium in the subsurface is reviewed, and relevant transport mechanisms are highlighted.

3. OCCURRENCE OF PLUTONIUM AND AMERICIUM IN THE SUBSURFACE

3.1 Atmospheric Deposition

Aboveground nuclear weapons tests between 1945 and 1975 have released about 360,000 Ci of plutonium (Carter and Moghissi 1977; Watters, Hakonson, and Lane 1983), mainly in the form of Pu-239, Pu-240, and Pu-238, as aerosol into the atmosphere, and this plutonium was subsequently deposited on the earth's surface. An additional atmospheric input occurred on April 21, 1964, when a satellite, carrying a Systems for Nuclear Activity Power generator (SNAP-9A) containing Pu-238, accidentally reentered the atmosphere, releasing about 16,000 Ci of plutonium (Hardy, Krey, and Volchok 1973; Watters, Hakonson, and Lane 1983). Monitoring showed that, by 1970, 95% of this plutonium had been deposited on the earth's surface, mostly in the Southern Hemisphere (Hardy, Krey, and Volchok 1973).

Plutonium also was released into the atmosphere during crashes of two airplanes carrying nuclear weapons—one in 1966 near Palomares, Spain, and one in 1968 near Thule, Greenland (Watters, Hakonson, and Lane 1983). Much of the released plutonium was recovered during cleanup operations; a portion, however, remained in the soil and sediment of affected areas.

As a result of the nuclear reactor accident at Chernobyl, Ukraine, on April 26, 1986, Pu-238, Pu-239, and Pu-240 were emitted into the atmosphere (Bunzl and Kracke 1990; Poyarkov et al. 2000 [Baryakhtar et al.]). Much of this plutonium was deposited on land surface, mainly in Belarus, Russia, and Ukraine, but other European countries, especially Scandinavian and Alpine countries, were affected as well (Poyarkov 2000 [Shestopalov and Poyarkov]). A major portion of radionuclides emitted was deposited in the night of April 27 because of rainfall in Sweden, Finland, Germany, Austria, Switzerland, Greece, Bulgaria, and Romania (Poyarkov 2000 [Shestopalov and Poyarkov]).

Following atmospheric deposition, fate and transport of plutonium are determined by a variety of environmental factors, such as type of vegetation, amount and characteristic of organic matter present in soil, soil type, and climatic conditions at the site. Migration of the center of the mass of atmospherically deposited plutonium and americium through soil proceeds very slowly. For instance, migration rates of about 1 cm per year have been reported for climatic conditions of southern Germany (Bunzl, Kracke, and Schimmack 1992; Bunzl and Kracke 1994). As the center of the mass of atmospheric deposition remains in upper soil layers worldwide, little can be inferred about transport rates in deeper soil horizons. Nevertheless, information about spatial distribution of atmospheric deposition of radionuclides provides useful insight about the environmental behavior of plutonium and americium.

Americium in the environment occurs mainly as the Am-241 isotope, which is produced by decay of Pu-241 (see Table 1) (Coughtrey et al. 1984, Vol. 5, pp. 1–235). The atmospheric distribution pattern of americium basically follows the pattern of Pu-241. Nuclear weapon explosions and nuclear fuel processing also directly have released americium into the environment (Coughtrey et al. 1984, Vol. 5, pp. 1–235).

Table 1. Selected nuclear properties of plutonium and americium (Seaborg and Loveland 1990; Lide 1994).

Element	Isotope	Decay Mode	Decay Energy (MeV)	Half-Life (year)	Decay Product
Plutonium	Pu-238	α	5.593	87.7	U-234
	Pu-239	α	5.244	24,110	U-235
	Pu-240	α	5.255	6,563	U-236
	Pu-241	β	0.021	14.4	Am-241
Americium	Am-241	α	5.637	432.7	Np-237

3.2 Direct Release to the Subsurface

Plutonium has been released directly to the subsurface either intentionally or accidentally. Intentional releases comprise underground nuclear bomb testing conducted by the United States, United Kingdom, France, China, and former Soviet Union, such as at the Nevada Test Site (Tamura 1975), Semipalatinsk Nuclear Test Site in Eastern Kazakhstan (Yamamoto et al. 1996), Novaya Zemlya (Carter and Moghissi 1977), Saharan Desert (Carter and Moghissi 1977), and Lop Nor in China (Carter and Moghissi 1977). Plutonium-containing waste was disposed of into the subsurface during liquid waste disposal procedures at nuclear production facilities, such as at Los Alamos, New Mexico (Nyhan et al. 1985; Penrose et al. 1990), Hanford, Washington (Rhodes 1957), Oak Ridge, Tennessee (UNIPUB 1982 [Garten, Trabalka, and Bogle]; Olsen et al. 1986), Idaho Falls, Idaho (UNIPUB 1982 [Rees and Cleveland]), Savannah River, South Carolina (Alberts, Halverson, and Orlandini 1986), Maxey Flats, Kentucky (Cleveland and Rees 1981), Karlsruhe, Germany (UNIPUB 1982 [Schuttelkopf and Pimpl]), Windscale and Sellafield, United Kingdom (Nelson and Lovett 1978), and Mayak Plutonium Production Plant in the former Soviet Union (Skipperud, Oughton, and Salbu 2000). Accidental releases occurred sporadically, such as during the explosion of a waste tank at the Mayak site (Skipperud, Oughton, and Salbu 2000), leakage of plutonium-contaminated oil from storage drums at Rocky Flats, Colorado (McDowell and Whicker 1978), or leaks in reactor cooling systems at Savannah River (Alberts, Halverson, and Orlandini 1986; Loyland et al. 2000).

Americium has been released through a similar pathway to that of plutonium—either directly from nuclear detonations or following radioactive decay of Pu-241. In addition to global atmospheric deposition, point-source releases of plutonium provide unintentional experiments on plutonium and americium fate and transport under different edaphic and climatic conditions.

3.3 Spatial Distribution of Plutonium and Americium in Soil

Measured depth distributions of plutonium and americium in soil indicate that two radionuclides sorb strongly to soil material and that translocation within soil is limited. The bulk of atmospheric deposited plutonium originating from weapons testing 30–40 years ago is usually found in the top 10–15 cm of soil (Harley 1980; UNIPUB 1982 [Yamamoto et al.]; UNIPUB 1982 [Yamamoto, Komurs, and Sakanoue]; Riekkinen and Jaakkola 2001). Figure 1 shows the depth distribution results from atmospheric deposition. The horizontal bars in Figure 1 represent measurement error (based on data from Bunzl et al. [1995]). Depth penetration of plutonium depends on climatic and edaphic conditions. For instance, in southern Germany (with a mean annual precipitation of 800 mm), more than 90% of the total discovered activity of plutonium and americium were located within the top 15 cm (Bunzl et al. 1995). Soil in which plutonium was released since the early 1940s from nuclear processing facilities at Hanford, Washington, (with a mean annual precipitation of 230 mm) contains 95% of Pu-239 and Pu-240 within the top 5 cm (Price 1991). Figure 2 displays distribution of plutonium with depth at Hanford for both offsite and onsite

locations (based on data from Price [1991]). Offsite locations are exposed to global atmospheric deposition only. Onsite locations have been exposed to emissions from nuclear facilities at the Hanford site in addition to global atmospheric deposition since the early 1940s. Plutonium from the nuclear explosion deposited in soil near Nagasaki (with a mean annual precipitation of 2,000 mm) on August 9, 1945, in the form of black rain is mostly (95% of inventory) contained in the top 20 cm of soil (Mahara and Miyahara 1984; Mahara and Kudo 1995).

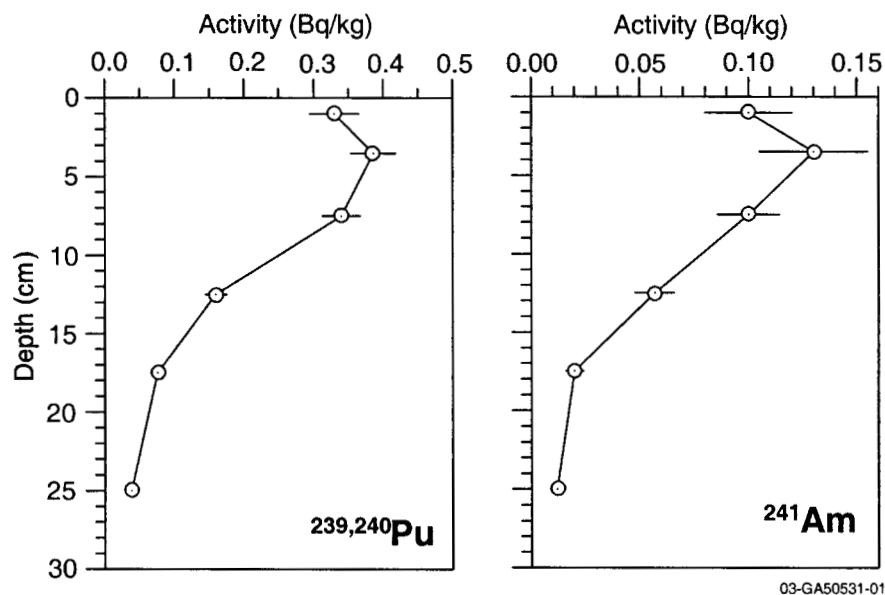


Figure 1. Depth distributions of Plutonium-239, Plutonium-240, and Americium-241 in an Alfisol under grassland in southern Germany resulting from atmospheric deposition.

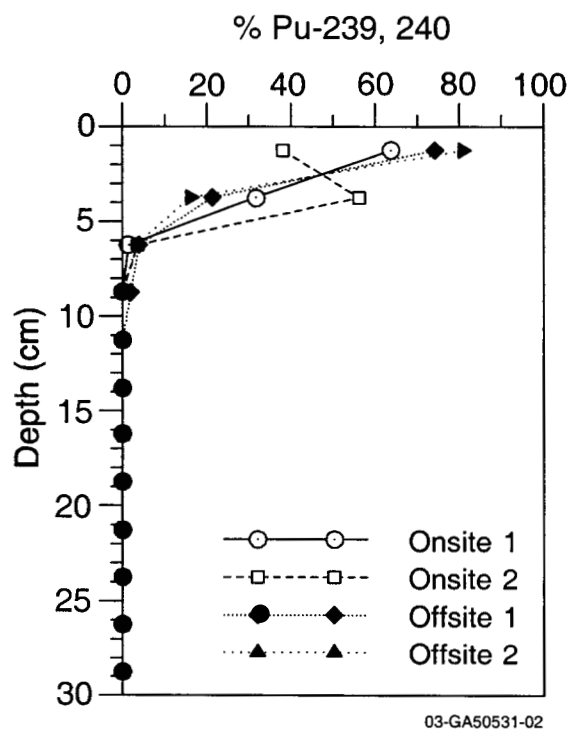
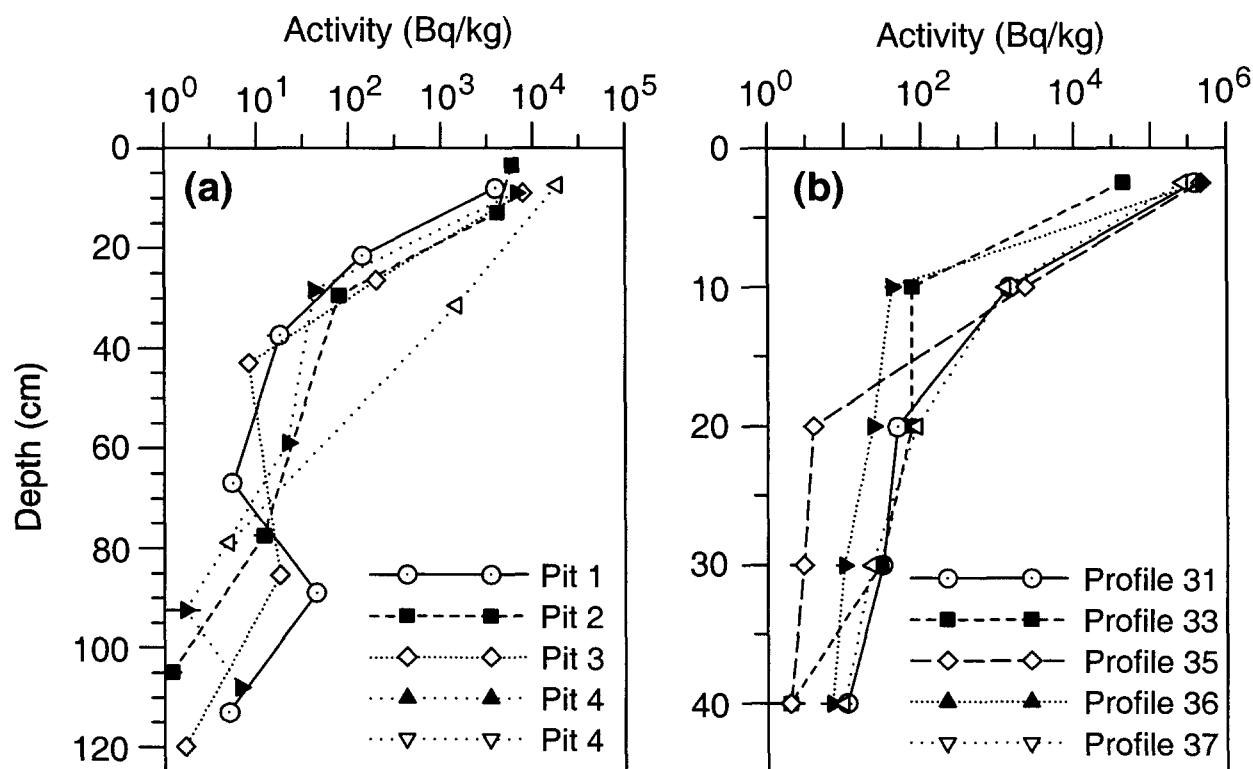


Figure 2. Depth distribution of Plutonium-239 and Plutonium-240 in soil at the Hanford site in Washington.

Although the bulk of plutonium remains in the very top of the soil, it has been found that a fraction of plutonium has moved to deeper locations in soil profiles. In soil at Nagasaki, 3% of the plutonium has migrated deeper than 30 cm and was detected to the maximum sampling depth of 4.5 m (Mahara and Kudo 1995). At Rocky Flats, Colorado, soil contaminated with atmospheric deposited plutonium originating from weapons processing has been detected at depths greater than 1 m. Figure 3 shows depth distribution origins of plutonium. Horizontal bars in Figure 3 represent measurement error (based on data from Litaor and Ibrahim [1996] and Iranzo et al. [1991]). Plutonium that was released as aerosol in 1966 when four thermonuclear bombs were dropped near Palomares, Spain, as a result of an aircraft accident (Iranzo et al. 1991; Rubio Montero et al. 2000; Rubio Montero and Sanchez 2001) moved to a depth of at least 45 cm in an uncultivated soil (see Figure 3). Some plutonium emitted by a reprocessing plant in Karlsruhe, Germany, had moved deeper than 20 cm in a sandy soil within less than 10 years (UNIPUB 1982 [Schuttelkopf and Pimpl]). Depth distributions of plutonium in soil surrounding Chernobyl showed that the center of the mass of plutonium was located between 1 and 15 cm deep, only 15 months after the accident, depending on soil type (Pavlotskaya et al. 1991). Deeper movement occurred mainly in soil with humus accumulations (Spodosols), implying humus complexation as potential translocation mechanisms.



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Figure 3. Depth distributions of Plutonium-239 and Plutonium-240 (a) originating from nuclear weapons processing between 1952 and 1989 and deposited by wind in soil at Rocky Flats, Colorado and (b) originating from aerosol deposition caused by an aircraft accident near Palomares, Spain, in 1966.

In special cases, plutonium and americium have been observed to move at faster rates than commonly observed in surface soil. At a waste disposal facility at Los Alamos, New Mexico, plutonium and americium were discharged through absorption beds, composed of 1.2-m-deep soil, sand, gravel, and stone, into unsaturated fractured tuff. After 33 years of operation, plutonium and americium were detected to depths of 6.5 and 13.4 m, respectively (Nyhan et al. 1985). In an adjacent absorption bed, where 20.5 m of water were applied in 1961 in order to move radionuclides through tuff, plutonium and americium were detected to the maximum sampling depth of 30 m (Nyhan et al. 1985). Additional application of water mobilized 3–49.6% of americium and 0.3–5.1% of plutonium present (Nyhan et al. 1985). A water application of 20.5 m in 1 year is admittedly a strong driving force for chemical movement. Nevertheless, the fact that plutonium and americium moved to a 30-m depth indicates that an accelerated movement of plutonium occurred. Such an accelerated movement can either be caused by preferential flow (fractured flow), colloid-facilitated transport, or a combination of both.

Plutonium activities in soil not only differ vertically, but plutonium activities also have considerable horizontal spatial variability. It has been observed that, particularly in deeper soil horizons, higher plutonium activities occur in preferential flow channels (Litaor, Barth, and Zika 1996; Bundt et al. 2000). This horizontal variability is a direct result of nonuniform flow pathways. However, even in the absence of preferential flow, plutonium tends to be distributed heterogeneously in soil, in part because some plutonium occurs as discrete particles in the form of PuO_2 (McDowell and Whicker 1978).

In aquatic ecosystems, plutonium and americium are accumulated in sediment layers of lakes and oceans (UNIPUB 1982 [Wahlgren and Orlandini]; UNIPUB 1982 [Yamamoto, Komurs, and Sakanoue]; Seaborg and Loveland 1990; Gasco et al. 2002; Michel et al. 2002). In contrast to terrestrial ecosystems, however, plutonium and americium are usually not found in the topmost layers of sediment but are distributed according to sedimentation patterns of the particular aquatic system. As a result, main plutonium and americium activities can occur at considerable depths below sediment surfaces (Michel et al. 2002) and, therefore, do not represent migration patterns of plutonium and americium through sediment but represent sedimentation rates (UNIPUB 1982 [Yamamoto, Komurs, and Sakanoue]; Michel et al. 2001).

While these monitoring studies allow scientists to assess spatial distributions and transport rates of plutonium and americium in the subsurface, little can be inferred about transport processes and mechanisms involved. Nevertheless, monitoring studies provide long-term, natural experiments that, in combination with more mechanistic studies, help people to better understand radionuclide fate and transport in their environment.

4. ISOTOPES OF PLUTONIUM AND AMERICIUM

Isotopes of plutonium vary from Pu-232 to Pu-246 and range in half-lives from about 1 minute to over 1,015 years. Almost all isotopes are α -emitters. Plutonium-239 has been found naturally in uranium deposits, occurring as a product of uranium radioactive decay, but has been estimated at a ratio of only one plutonium atom per 10^{11} uranium atoms (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]). The long-lived Pu-244 isotope also has been identified in very small quantities. Therefore, the source of plutonium isotopes both in the environment and for the chemistry laboratory is nuclear synthesis. Of the synthesized isotopes, Pu-239 is the most important both for production of nuclear weapons and fuel. Some nuclear properties of major plutonium isotopes are summarized in Table 1.

Americium isotopes include mass numbers from Am-234 to Am-247. Most heavier forms have half-lives around 20 minutes and are β -emitters. Americium-241 and Am-243 are α -emitting radioisotopes and are the most important in terms of quantities produced in power reactors. They originate from irradiation of Pu-239 and decay of Pu-241 (Am-241) and Pu-242 (Am-243). Half-lives of Am-241 and Am-243 are 432.7 and 7,380 years, respectively (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]). Americium is used in sealed sources in scientific instruments and smoke detectors, but these uses are small compared to nuclear reactor and weapon sources (Zhang and Brady 2002 [Zhang, Krumhansl, and Brady]).

Isotopic ratios among different plutonium isotopes and among plutonium isotopes with other radionuclides have been used to determine the origin of plutonium contamination found in the environment (Cochran et al. 2000; Dasher et al. 2002; Huh 1997; Mitchell et al. 1997; Kersting et al. 1999). Each nuclear weapon test released specific Pu-240 and Pu-239 isotopic ratios, and these ratios have been used to identify sources of plutonium found in the environment (Kersting et al. 1999; Muramatsu et al. 2001). Similarly, Am-241, Pu-239, and Pu-240 ratios have been used to identify origins of plutonium contamination (UNIPUB 1982 [Yamamoto, Komurs, and Sakanoue]). Americium-241, Pu-239, and Pu-240 activity ratios in sequential extractions were used to infer that radionuclides moved from ocean sediment to the water column (Haque and Nakanishi 1999). Baskaran et al. (1996) measured Pu-238, Pu-239, Pu-240, Cs-137, and excess Pb-210 concentrations in surficial sediment and sediment cores from the Ob and Yenisey Rivers (located in Russia) and the Kara sea to show that >95% of radioisotopes came from fallout.

5. GEOCHEMISTRY OF PLUTONIUM AND AMERICIUM

5.1 Oxidation States

Plutonium has multiple oxidation states under environmental conditions (see Table 2). Plutonium(III) is unstable under most environmental conditions and easily oxidized; Pu(IV) is the most stable state in water that contains significant amounts of organic material; Pu(V) is the stable state in water without organic material (Seaborg and Loveland 1990). In the presence of humic materials, Pu(V) is reduced to Pu(IV). Stable soluble species are Pu(V) and Pu(VI); however, under most environmental conditions, Pu forms insoluble phases with inorganic anions, such as OH^- , CO_3^{2-} , HPO_4^{2-} , F^- , and SO_4^{2-} , and with organic materials resulting in accumulation in sediment (Seaborg and Loveland 1990). Hydrolysis and complexation decrease in the order $\text{Pu}^{4+} > \text{PuO}_2^{2+} > \text{Pu}^{3+} > \text{PuO}_2^+$ (Seaborg and Loveland 1990) following the effective charge $+4 > +3.2 > +3 > +2$ on the ions (Cleveland 1979). The oxidation state of plutonium is affected by all of these reactions—oxidation and reduction (determined by Eh and pH), precipitation and dissolution of insoluble solid phases, and formation of inorganic and organic complexes (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]).

Table 2. Selected chemical and physical properties of plutonium and americium ions.

Oxidation State	Form ^a	Ionic Radius ^b (nm)
Plutonium		
III	Pu^{3+}	0.0997
IV	Pu^{4+}	0.0887
IV	$\text{PuO}_2 \cdot n\text{H}_2\text{O}$	NA
V	PuO_2^+	NA
VI	PuO_2^{2+}	NA
Americium		
III	Am^{3+}	0.0982

a. Weigle et al. (1986)
b. Seaborg and Loveland (1990)

The redox chemistry of plutonium is unique in the sense that substantial concentrations of common oxidation states, Pu(III), Pu(IV), Pu(V), and Pu(VI), can coexist in the same solution (Cleveland 1970; Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]). This behavior is due to both thermodynamic and kinetic considerations. From a thermodynamic standpoint, reduction potentials of various redox couples are often similar in particular solutions (see Figure 4) (Choppin 1999). Thus, in acid solutions, where reduction potential relative to standard hydrogen electrode is near one for all couples shown in Figure 4, plutonium can exist in four oxidation states simultaneously at equilibrium. Disproportionation reactions, $\text{Pu(IV)} \rightarrow \text{Pu(III)} + \text{Pu(VI)}$ and $\text{Pu(V)} \rightarrow \text{Pu(IV)} + \text{Pu(VI)}$, result in redistribution of plutonium species if the reaction is favored by solution conditions. For example, Pu(V) undergoes disproportionation in acid solutions but is the stable species in neutral and basic solutions (Choppin 1999).

The redox speciation of plutonium is important from an environmental standpoint because of differences in behavior of various species. Plutonium(III) and Pu(IV) states exist as Pu^{3+} and Pu^{4+} cations in aqueous solutions and are strongly sorbed to soil and sediment. Of these two species, Pu(IV) is dominant in neutral and alkaline media except under suboxic and anoxic conditions (Choppin, Bond, and

Hromadka 1997). In this oxidation state, plutonium is particularly immobile in the subsurface because of its tendency to sorb strongly to natural minerals and organic matter and to form extremely insoluble $\text{Pu}(\text{OH})_4$ and $\text{PuO}_2(\text{c})$ solid phases. The equilibrium constant for $\text{PuO}_2(\text{c})$ dissolution from free energies of $\text{PuO}_2(\text{c})$, $\text{Pu}^{4+}(\text{aq})$, H_2O , and $(\text{OH}^-)(\text{aq})$ has been calculated to be $\log K = -63.3$ for the reaction (Katz and Seaborg 1986 [Morss]) shown in Equation (1).



Pu(III) — Pu(IV) — Pu(V) — Pu(VI)				pH
0.982 V	1.170 V	0.916 V		0
-0.39 V	0.70 V	0.60 V		8
-1.04 V	0.52 V	0.16 V		14
		1.043 V		0
		0.65 V		8
		0.34 V		14

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Figure 4. Reduction potentials between the couples of Pu(III) through Pu(VI) determined in noncomplexing media at acid, neutral, and basic pH.

Solubility of $\text{Pu}(\text{OH})_3(\text{c})$ also is estimated to be low ($\log K = -22.6$) as is that of $\text{Am}(\text{OH})_3(\text{c})$ ($\log K = -24$) (Katz and Seaborg 1986 [Morss]). In spite of extremely low solubility, the total concentration of Pu(IV) species still may be significant in aqueous solutions in equilibrium with $\text{PuO}_2(\text{c})$ or with somewhat-more-soluble $\text{Pu}(\text{OH})_4(\text{s})$ ($\log K = 55$) (Choppin, Bond, and Hromadka 1997). This is because Pu(IV) forms stable complexes with hard inorganic ligands such as F, CO_3 , PO_4 , and SO_4 (Katz and Seaborg 1986 [Ahrland]) and is complexed by dissolved humic materials (Choppin, Bond, and Hromadka 1997). Furthermore, hydrolyzed species forms hydroxy and, eventually, oxopolymers that can grow to colloidal size before forming a crystalline precipitate. Thus, the concentration of Pu(IV) in aqueous solution is likely to be much higher than that of the hydrated $\text{Pu}^{4+}(\text{aq})$ ion. Nevertheless, most Pu(III), Am(III), and Pu(IV) in the environment are associated with solid phases either through (1) precipitation of hydroxide or oxide or (2) through sorption to geologic media by chemisorption or ion exchange (Carnall 1983).

Plutonium(V) and Pu(VI) oxidation states, on the other hand, are less strongly associated with solid phases. This is especially true of $\text{Pu}(\text{V})\text{O}_2^+$, which behaves similarly to a monovalent spherical cation. It is complexed only weakly in solution and associates with surfaces through cation exchange with relatively low selectivity. The tendency to form surface complexes with geologic media follows the same order as that of hydrolysis, $\text{Pu}^{4+} > \text{PuO}_2^{2+} > \text{Pu}^{3+} > \text{PuO}_2^+$.

Humic substances can participate in oxidation-reduction reactions with plutonium as reviewed by Choppin (1988) and Kudo (2001) (Choppin and Morgenstern). Reduction appears to be governed by hydroquinone groups while oxidation can occur indirectly when humic materials undergo photolysis under UV light and produce hydrogen peroxide. Reduction of Pu(VI) to Pu(IV) has been shown to proceed rapidly under laboratory conditions, and reduction to Pu(III) also can occur under suboxic conditions or under aerobic conditions when the pH is below 3.

Possible oxidation states of americium are Am(III), Am(IV), Am(V), and Am(VI), but, under environmental conditions, americium occurs only as Am(III) (Seaborg and Loveland 1990). Consequently, the environmental chemistry of americium is much simpler than that of plutonium. Americium(III) is considered to behave very similarly to Pu(III) and is often used as an analogue for Pu(III).

5.2 Hydrolysis

Although OH^- can be treated strictly as a ligand, in this case, its reaction will be treated with plutonium from the viewpoint of the hydrolysis reaction or the dissociation of H_2O molecules in the inner sphere of the aqueous plutonium species. The analysis in Section 5.3 asserts that OH^- ligand can be replaced by other species such as CO_3^{2-} and F^- .

5.2.1 Plutonium(III) and Americium(III)

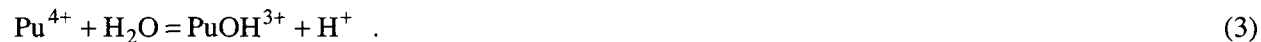
Reliable values for the first hydrolysis constant of Pu(III) are difficult to obtain because of the problem of oxidation to Pu(IV) and subsequent precipitation. The ionic radius of Pu(III) is 1.00 Å. Therefore, it should be a relatively weak acid. For the reaction shown in Equation (2), the log K has been reported as high as -3.8 and as low as -6.95 (Katz and Seaborg 1986 [Ahrland]).



For Am(III), which has an ionic radius of 0.98 Å, direct measurement by titration yielded a value of -7.5 (Rai et al. 1983). Katz and Seaborg (1986) (Ahrland) argue that actinides should be comparable in acidity to lanthanides, whose first hydrolysis constants range from log $K = -8.3$ (La^{3+}) to -7.6 (Lu^{3+}). This argument, along with the value reported for Am(III), would seem to support a log K near -7.5 ; however, in a recent compilation of thermodynamic data by the Japan Nuclear Cycle Development Institute, Kudo (2001) (Yui et al.) selects a value of log $K = -6.4$ for Am(III) and, by analogy, also for Pu(III) (see Table 3).

5.2.2 Plutonium(IV)

Tetravalent Pu^{4+} hydrolyzes easily in solution as a result of its high charge and small radius (0.89 Å). Log $K = -0.5$ for the reaction shown in Equation (3) is reported by both Baes and Mesmer (1976) and Kudo (2001) (Yui et al.).



As pH increases, soluble Pu(IV) disproportionates to form other oxidation states, (Pu[III], Pu[V], and Pu[VI]) and Pu(IV) cation precipitates to form $\text{PuO}_2(\text{s})$, which is extremely insoluble, whether in an amorphous form as reported above or in its crystalline form (see Figure 5 and Table 3). The diagrams in Figure 5 were created by Larry Hull based on thermodynamic data from Delany and Lundeen (1990) and Lemire et al. (2001).

Table 3. Equilibrium constants for Plutonium(IV), Plutonium(V), Plutonium(VI), and Americium(III) solid dissolution, aqueous inorganic formation, and reduction reactions.

Reaction	Log K
Plutonium(IV)	
$\text{PuO}_2(\text{cr}) + 2\text{H}_2\text{O} = \text{Pu}^{4+} + 4\text{OH}^-$	-63.30 ^a
$\text{PuO}_2(\text{am}) + 2\text{H}_2\text{O} = \text{Pu}^{4+} + 4\text{OH}^-$	-56.85
$\text{Pu}^{4+} + 2\text{H}_2\text{O} = \text{PuOH}^{3+} + \text{H}^+$	-0.50
$\text{Pu}^{4+} + \text{SO}_4^{2-} = \text{PuSO}_4^{2+}$	9.00
$\text{Pu}^{4+} + 2\text{SO}_4^{2-} = \text{Pu}(\text{SO}_4)_2^0$	11.70
$\text{Pu}^{4+} + 5\text{CO}_3^{2-} = \text{Pu}(\text{CO}_3)_5^{6-}$	34.18
$\text{Pu}^{4+} + 2\text{CO}_3^{2-} + 2\text{OH}^- = \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$	44.76
$\text{Pu}^{4+} + \text{e}^- = \text{Pu}^{3+}$	16.99
Plutonium(V)^a	
$\text{PuO}_2(\text{OH})(\text{am}) = \text{PuO}_2^+ + \text{OH}^-$	-8.79
$\text{NaPuO}_2\text{CO}_3(\text{cr}) = \text{Na}^+ + \text{PuO}_2^+ + \text{CO}_3^{2-}$	-11.00
$\text{Na}_3\text{PuO}_2(\text{CO}_3)_2(\text{cr}) = 3\text{Na}^+ + \text{PuO}_2^+ + 2\text{CO}_3^{2-}$	-14.32
$\text{PuO}_2^+ + \text{OH}^- = \text{PuO}_2(\text{OH})^0$	2.70
$\text{PuO}_2^+ + 2\text{OH}^- = \text{PuO}_2(\text{OH})_2^-$	4.35
$\text{PuO}_2^+ + \text{CO}_3^{2-} = \text{PuO}_2(\text{CO}_3)^-$	4.90
$\text{PuO}_2^+ + \text{Cl}^- = \text{PuO}_2\text{Cl}^0$	0.70
$\text{PuO}_2^+ + \text{NO}_3^- = \text{PuO}_2\text{NO}_3^0$	1.10
$\text{PuO}_2^+ + \text{F}^- = \text{PuO}_2\text{F}^0$	1.90
$\text{PuO}_2^+ + \text{HPO}_4^{2-} = \text{PuO}_2\text{HPO}_4^-$	3.40
$\text{PuO}_2^+ + \text{H}_2\text{PO}_4^- = \text{PuO}_2\text{H}_2\text{PO}_4^0$	1.50
$\text{PuO}_2^+ + \text{SO}_4^{2-} = \text{PuO}_2\text{SO}_4^-$	2.00
$\text{PuO}_2^+ + \text{e}^- + 4\text{H}^+ = \text{Pu}^{4+} + 2\text{H}_2\text{O}$	18.60
Plutonium(VI)	
$\text{PuO}_2^{2+} + \text{Cl}^- = \text{PuO}_2\text{Cl}^+$	0.10
$\text{PuO}_2^{2+} + \text{F}^- = \text{PuO}_2\text{F}^+$	4.57
$\text{PuO}_2^{2+} + 2\text{F}^- = \text{PuO}_2\text{F}_2^0$	8.24
$\text{PuO}_2^{2+} + 3\text{F}^- = \text{PuO}_2\text{F}_3^-$	9.80
$\text{PuO}_2^{2+} + \text{H}_2\text{O} = \text{PuO}_2\text{OH}^+ + \text{H}^+$	-5.27
$\text{PuO}_2^{2+} + 2\text{H}_2\text{O} = \text{PuO}_2(\text{OH})_2^0 + 2\text{H}^+$	-12.46
$\text{PuO}_2^{2+} + 3\text{H}_2\text{O} = \text{PuO}_2(\text{OH})_3^- + 3\text{H}^+$	-24.67
$\text{PuO}_2^{2+} + \text{NO}_3^- = \text{PuO}_2\text{NO}_3^+$	0.30
$\text{PuO}_2^{2+} + \text{CO}_3^{2-} = \text{PuO}_2\text{CO}_3^0$	9.56
$\text{PuO}_2^{2+} + 2\text{CO}_3^{2-} = \text{PuO}_2(\text{CO}_3)_2^{2-}$	15.00
$\text{PuO}_2^{2+} + 3\text{CO}_3^{2-} = \text{PuO}_2(\text{CO}_3)_3^{4-}$	17.53
$\text{PuO}_2^{2+} + \text{HPO}_4^{2-} = \text{PuO}_2\text{HPO}_4^0$	7.24 ^b

Table 3. (continued).

Reaction	Log <i>K</i>
$\text{PuO}_2^{2+} + \text{H}_3\text{PO}_4^0 = \text{PuO}_2\text{H}_2\text{PO}_4^+ + \text{H}^+$	1.12 ^b
$\text{PuO}_2^{2+} + \text{SO}_4^{2-} = \text{PuO}_2\text{SO}_4^0$	3.15 ^b
$\text{PuO}_2^{2+} + 2\text{SO}_4^{2-} = \text{PuO}_2(\text{SO}_4)_2^{2-}$	4.14 ^b
$\text{PuO}_2^{2+} + \text{e}^- = \text{PuO}_2^+$	16.16
Americium(III)	
$\text{Am}(\text{OH})_3(\text{am}) = \text{Am}^{3+} + 3\text{OH}^-$	-25.00
$\text{Am}(\text{OH})_3(\text{cr}) = \text{Am}^{3+} + 3\text{OH}^-$	-26.80
$\text{Am}_2(\text{CO}_3)_3(\text{cr}) = 2\text{Am}^{3+} + 3\text{CO}_3^{2-}$	-33.40
$\text{AmOHCO}_3(\text{cr}) = \text{Am}^{3+} + \text{OH}^- + \text{CO}_3^{2-}$	-22.50
$\text{NaAm}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{cr}) = \text{Na}^+ + \text{Am}^{3+} + 2\text{CO}_3^{2-} + 6\text{H}_2\text{O}$	-21.40
$\text{AmPO}_4 \cdot n\text{H}_2\text{O}(\text{am}) = \text{Am}^{3+} + \text{PO}_4^{3-} + n\text{H}_2\text{O}$	-24.79
$\text{AmF}_3(\text{cr}) = \text{Am}^{3+} + 3\text{F}^-$	-19.50
$\text{Am}^{3+} + \text{H}_2\text{O} = \text{AmOH}^{2+} + \text{H}^+$	-6.40
$\text{Am}^{3+} + 2\text{H}_2\text{O} = \text{Am}(\text{OH})_2^+ + 2\text{H}^+$	-14.10
$\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3^0 + \text{H}^+$	<-28.60
$\text{Am}^{3+} + \text{F}^- = \text{AmF}^{2+}$	3.40
$\text{Am}^{3+} + 2\text{F}^- = \text{AmF}_2^+$	5.80
$\text{Am}^{3+} + 3\text{F}^- = \text{AmF}_3^0$	<11.20
$\text{Am}^{3+} + \text{CO}_3^{2-} = \text{AmCO}_3^+$	7.60
$\text{Am}^{3+} + 2\text{CO}_3^{2-} = \text{Am}(\text{CO}_3)_2^-$	12.30
$\text{Am}^{3+} + 3\text{CO}_3^{2-} = \text{Am}(\text{CO}_3)_3^{3-}$	15.20
$\text{Am}^{3+} + \text{H}_2\text{PO}_4^- = \text{AmH}_2\text{PO}_4^{2+}$	2.74
a. Katz and Seaborg 1986; the log <i>K</i> s are based on analogy of Np(V).	
b. The log <i>K</i> s are based on analogy of U(VI).	

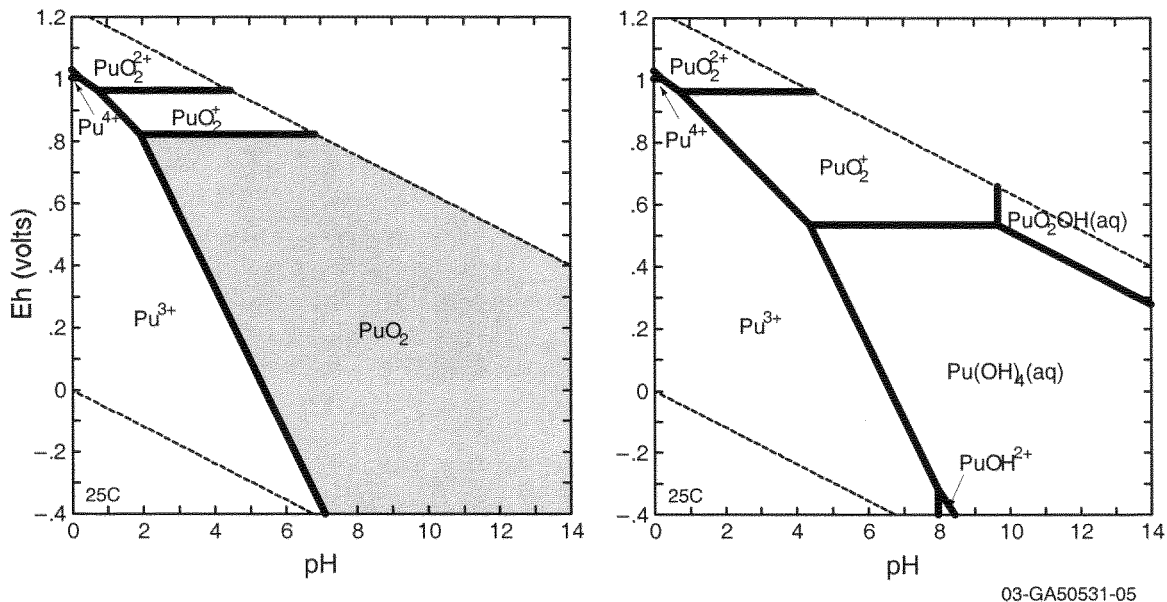


Figure 5. The Eh-pH diagram for (1) plutonium species in equilibrium with PuO_2 solid phase at 25°C and 1.013 bars and (2) aqueous plutonium species at 25°C and 1.013 bars .

5.2.3 Plutonium(V)

Pu(V) in water (PuO_2^+), with its low effective charge, is hydrolyzed only in highly alkaline solutions. The concentration constant ($\log {}^cK$) in 10^{-3} molal chloride solution has been reported as -9.6 (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]; Katz and Seaborg 1986 [Arhland]; Baes and Mesmer 1976). Kudo (2001) (Yui et al.) chose a thermodynamic equilibrium constant ($\log K$) of -11.3 based on analogy with NpO_2^+ for the Japan Nuclear Cycle Development Institute database. The difference between these values is too large to be due to the difference in activity coefficients between chloride solutions, so considerable uncertainty is in the $\log K$ for this reaction:



This value will only be important in environmental solutions with $\text{pH} > 8$ when complexation with CO_3^{2-} will become a competing reaction (see Figure 6). In Figure 6, plutonium concentrations were fixed at 10^{-5} molal, $a(\text{HCO}_3^-) = 10^{-2.63}$, $a(\text{F}^-) = 10^{-3.96}$, $a[\text{SiO}_2(\text{aq})] = 10^{-3.3}$. Figure 6 was created by Larry Hull based on thermodynamic data from Delany and Lundeen (1990) and Lemire et al. (2001).

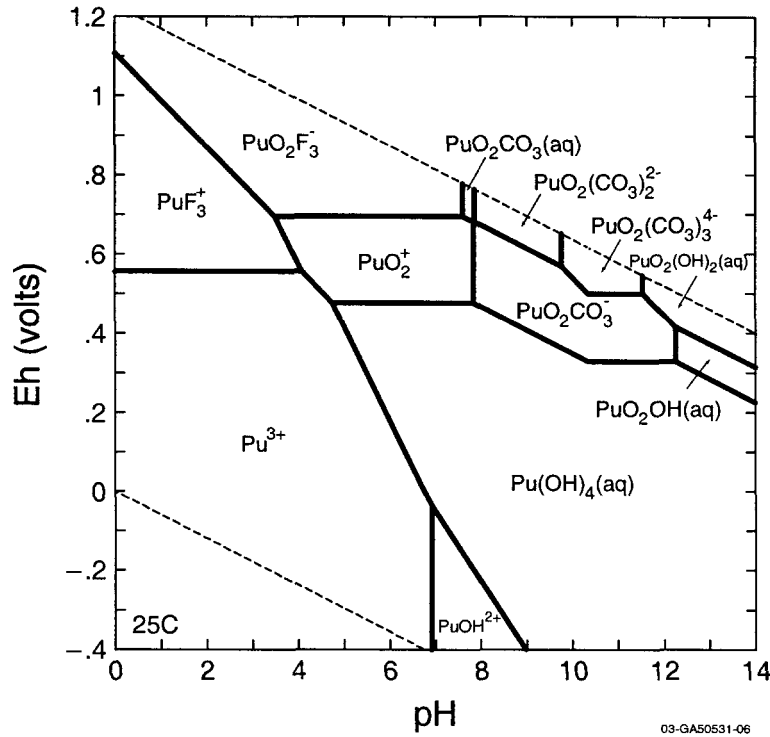


Figure 6. The Eh-pH diagram for plutonium in water containing hydroxide, carbonate, and fluoride ions representative for Well J-13 from Yucca Mountain, Nevada (25°C, 1.013 bars).

5.2.4 Plutonium(VI)

Plutonium(VI) is strongly hydrolyzed. The first hydrolysis constant for the reaction shown in Equation (5) has been reported to be as high as $\log K = -3.3$ and as low as $\log K = -5.97$ (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]).



Most reported values are concentration constants and depend on the ionic strength and composition of the solution in which they are determined. In the compilation of Kudo (2001) (Yui et al.), corrections have been made using Pitzer ion interaction coefficients to obtain thermodynamic equilibrium constants from the best data available. In Table 3, Am(III) is used as an analogue for Pu(III). All data are from the thermodynamic database selected and developed by Kudo (2001) (Yui et al.). Indirect evidence from both spectroscopic and titration data reveals that PuO_2^{2+} can form dimers and trimers. The dimer ($[\text{PuO}_2]_2[\text{OH}]_2^{2+}$) and trimer ($[\text{PuO}_2]_3[\text{OH}]_3^{+}$) are likely candidates, and estimated $\log^\circ K$ s are -8.36 and -21.65 , respectively (Baes and Mesmer 1976; Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]), for reactions of this form:



5.3 Complexation

5.3.1 Inorganic Complexes

All oxidation states of plutonium cations behave as hard Lewis acid; therefore, they form primarily ionic and electrostatic bonds with hard Lewis bases (Katz and Seaborg 1986 [Arhland]). The order of decreasing tendency for complex formation is $\text{Pu}^{4+} > \text{PuO}_2^{2+} > \text{Pu}^{3+} > \text{PuO}_2^+$, the same as for hydrolysis. The hard-hard interaction also is reflected by the following affinity order of the monovalent inorganic ligands: $\text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$ although Cl^- and NO_3^- affinities are reversed for PuO_2^{2+} . For hard, divalent ligands, the order $\text{CO}_3^{2-} > \text{oxalate} > \text{SO}_4^{2-}$ is followed with these complexes generally stronger than those with monovalent ligands (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]).

The Eh-pH diagram shown in Figure 6 includes both F^- and CO_3^{2-} complexes with plutonium. These complexes are most important under conditions at the edges of Eh and pH values relevant to natural waters (see Figure 6). Fluoride complexes with Pu^{4+} are stable under oxidizing conditions below pH 4, and the $\text{PuO}_2\text{CO}_3^-$ complex is stable in oxidizing alkaline solutions. Higher concentrations of inorganic ligands could stabilize inorganic complexes with these or other ions, but such concentrations are not generally found in natural systems (Kudo 2001 [Choppin and Morgenstern]). Nash, Cleveland, and Rees (1988) found a positive correlation between plutonium solubility and carbonate and fluoride concentrations when their concentrations were high. They also stated that this result was not in agreement with thermodynamic predictions of complex formation, indicating that current equilibrium constants for these complexes are less than certain. A fairly recent study of Pu(IV) complexation with CO_3^{2-} indicates that earlier determinations of the stability of the first monomeric complex were overestimated (Nitsche and Silva 1996). As a result, the amount of plutonium-carbonate complexation may be overstated in earlier publications.

In most natural waters, inorganic complexes with most oxidation states of plutonium are unlikely to dominate their solution speciation because stability constants are not high enough for complexation to play an important role (Kudo 2001 [Choppin and Morgenstern]). The strongest complexes are formed with Pu(IV), and it is clear that inorganic Pu(IV) speciation in solution will be dominated by hydrolysis. Although formation of the carbonate complex may not often affect solubility of plutonium in natural waters, Nitsche et al. (1992) found evidence that high carbonate water from the Yucca Mountain site in Nevada may stabilize Pu(IV) in solution, relative to other plutonium oxidation states.

Americium is also a hard Lewis acid and forms complexes with the same Lewis bases as plutonium. The order for the monovalent anions is $\text{F}^- > \text{H}_2\text{PO}_4^- > \text{SCN}^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$ (Katz and Seaborg 1986 [Shulz and Penneman]). The stability of Am^{3+} complexes can be estimated from complexes with trivalent lanthanides with similar radii, but americium-ligand bonds tend to be somewhat larger because of some covalency from 5f electrons.

Americium complexation with inorganic ions is to be likely more important than in the case of plutonium because of the stable +3 oxidation state for americium. This species forms relatively strong complexes, with carbonate in particular (Clark, Hobart, and Neu 1995), and the $\text{AmOHCO}_3(\text{s})$ solid phase may be limiting in some natural systems (Nash, Cleveland, and Rees 1988; Nitsche et al. 1992). Nitsche et al. (1992) found increased Am(III) solubility with increasing carbonate content, possibly, because of soluble Am- CO_3 complexes and suggested $\text{AmOHCO}_3(\text{s})$ as the limiting solid phase. Under most pH and Eh conditions found in environmental systems, americium in solution is dominated by Am^{3+} , americium carbonates, and americium hydroxycarbonates (see Figure 7). Figure 7 was created by Larry Hull based on thermodynamic data from Delany and Lundeen (1990) and Silva et al. (1995). Nash, Cleveland, and Rees (1988) provide evidence that CO_3^{2-} enhances Am(III) solubility in many carbonate-containing waters.

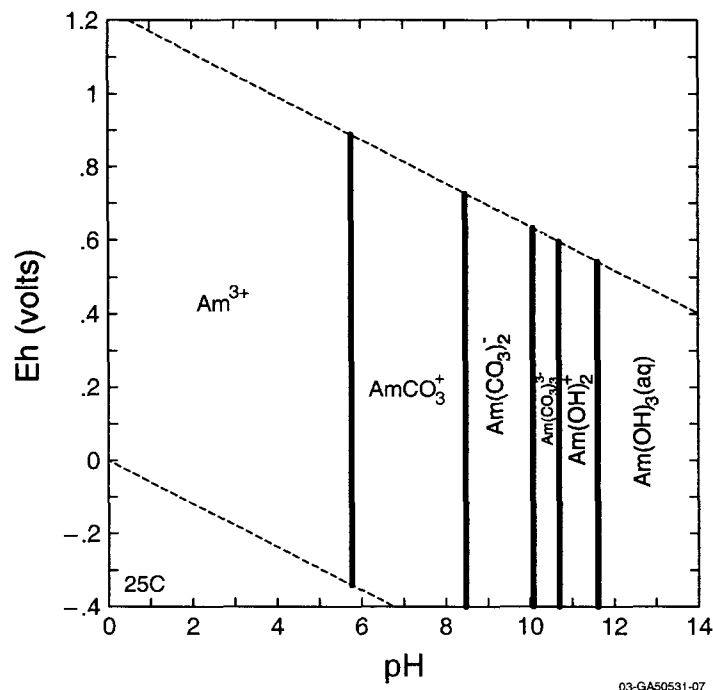


Figure 7. The Eh-pH diagram for aqueous americium species at 25°C and 1.013 bars ($a[\text{Am}] = 10^{-5}$, $a[\text{HCO}] = 10^{-2.63}$).

5.3.2 Organic Complexes

Complexation of plutonium by organic molecules is dominated by hard-hard interactions as in the case of inorganic complexes; thus, the most important functional groups will be OH groups associated with carboxylate and phenolic moieties. The order of binding strength in terms of oxidation state is the same as given above for inorganic complexes (Katz and Seaborg 1986 [Arhland]). By analogy, Am(III) behaves like Pu(III) and PuO_2^{2+} in terms of complexation with organic ligands. Stability complexes with the same ligands are often the same between Am(III) and either Pu(III) or PuO_2^{2+} , which are also similar in binding strength to the same functional groups (Katz and Seaborg 1986 [Arhland]). Complexation with a single carboxylate group is somewhat weaker than with an inorganic carbonate group, but, when the organic molecule contains several functional groups able to bond simultaneously with plutonium, much stronger complexes are formed (Katz and Seaborg 1986 [Arhland]). Chelate formation can take place with organic ligands specifically added to process streams to complex plutonium (e.g., ethylenediaminetetraacetic acid [EDTA] and nitrotetraacetic acid [NTA]) and with natural organic compounds found in groundwater and in the vadose zone, namely humic materials (Katz and Seaborg 1986 [Arhland]; Kudo 2001 [Choppin and Morgenstern]).

Chelating agents, such as EDTA or NTA, form strong complexes with actinide ions (Seaborg and Loveland 1990). Strong potential for complexation with organic ligands will increase apparent solubility of actinides in aqueous solution. Complexes with EDTA and NTA have repeatedly been found to increase concentrations of plutonium in environmental waters (UNIPUB 1982 [Rees and Cleveland]; Al Mahamid et al. 1996; Sylwester 2001). For instance, Cleveland and Rees (1981) found that dissolved-Pu(IV)-EDTA complexes were the primary plutonium species of leachates from the Maxey Flats radioactive trenches in Kentucky. The dominant oxidation state of plutonium in the presence of EDTA and NTA, measured over a large range of plutonium and organic ligand ratios at pH 5–8, was found to be Pu(IV). Plutonium(III)

was oxidized, and Pu(V) and Pu(VI) were reduced by organic ligands (Al Mahamid et al. 1996). The most stable of the plutonium-EDTA complexes, Pu(IV) EDTA, is about 10–20 orders of magnitude greater than EDTA complexes with transition metals, lanthanides, and alkaline earth metals (Means and Alexander 1981). Of all complexing agents tested, EDTA forms the most stable complexes with plutonium and out-competes alkali, earth alkali, and transition metals (Cleveland 1979). Incidentally, because of its great chelating ability, EDTA is used to remove plutonium ingested by humans (Means and Alexander 1981).

In the absence of synthetic chelates, such as EDTA and NTA, plutonium and americium will interact with natural organic molecules, which are dominated by humic substances (Kudo 2001 [Choppin and Morgenstern]). In what is strictly an operational definition, humic materials consist of humic acid and fulvic acid, which are extractable by strong base, and humin, which is not. Humic acid precipitates from aqueous solution at pH 3, and fulvic acid remains in solution. Generally, fulvic acid is made of smaller molecular-weight molecules with more titratable functional groups and more aliphatic character compared to humic acid.

Interaction between plutonium and americium with humic and fulvic acid has important effects on the behavior of both elements in the environment. These interactions can affect distribution between the solution and solid phase, the oxidation state of plutonium, and the transport of both colloidal and soluble species (Kudo 2001 [Choppin and Morgenstern]). Nelson et al. (1985) showed that plutonium sorption to suspended sediment particles was inhibited by association with organic material while others have shown that actinides and organic molecules may simultaneously sorb to inorganic particles (Righetto et al. 1991) forming pseudocolloids that may enhance associated radionuclide transport (Buckau, Stumpe, and Kim 1986; Kudo 2001 [Choppin and Morgenstern]). Fulvic acid did not appear to enhance solubility of plutonium or americium in contaminated soil (Cleveland and Rees 1976), but this may be due to the fact that much stronger complexes are formed with higher molecular-weight carbon compounds (Agapkina et al. 1995; Choppin 1988). McCarthy, Sanford, and Stafford (1998) showed that lanthanide transport was enhanced in groundwater at Oak Ridge National Laboratory in the presence of dissolved organic matter, but, in its absence, americium was strongly sorbed by the same matrix. Soluble americium and plutonium sampled from a contaminant plume were determined by anion exchange separation to be anionic in nature and associated with soluble organic complexes (Cooper, Haas, and Mattie 1995).

5.4 Polymerization

The plutonium polymer consists of Pu^{4+} linked by oxide and hydroxide bridges. It can be formed either by degradation of Pu(IV) hydroxide or by hydrolysis of Pu^{4+} ions in solution. Because of the concern that plutonium could be concentrated during processing, the formation and stability of the plutonium polymer have been extensively studied. Lloyd and Haire (1978) synthesized and characterized the polymer by both pathways in a variety of solutions and conditions. The polymer is bright green in color, consists of discrete particles generally less than 20 Å in diameter, and carries little net charge (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]). Stability of the polymers depends on aging where particles transform to a more crystalline state (Lloyd and Haire 1978; Kudo 2001 [Choppin and Morgenstern]). Depolymerization can be enhanced by adding complexing ligands, such as F^- or SO_4^{2-} , to the solution. Rundberg et al. (1988) have studied size and density of the plutonium colloid, and Silver (1983) has calculated a free energy for its formation.

Plutonium(IV) polymerization has been studied extensively under conditions expected in processing streams. These solutions have high ionic strength, usually nitrate salts, and high acidity. Simple dilution is enough to lower acidity to the point where polymerization occurs (Katz and Seaborg 1986 [Weigel, Katz, and Seaborg]). Fewer studies exist on polymerization under environmental conditions of low Pu(IV) concentration and low ionic strength. Given the low solubility of PuO_2 , such polymers could

form in the environment. Polymer formation will enhance the apparent solubility of plutonium if the polymers are small enough in size to form stable colloidal suspensions.

5.5 Sorption to Subsurface Materials

5.5.1 Macroscopic Sorption Behavior

Several studies have been performed to evaluate the sorption of plutonium to subsurface materials or to pure minerals. Less work has been carried out with americium, yet its behavior is somewhat better understood because of its single oxidation state in natural systems. Examples of many materials examined for plutonium and americium sorption are corroded high-level waste glass (Luckscheiter and Kienzler 2001); clay minerals (Nagasaki, Tanaka, and Suzuki 1997a); calcium carbonate (Nelson, Orlandini, and Penrose 1989); iron oxides (Sanchez, Murray, and Sibley 1985); alumina (Righetto et al. 1988); groundwater colloids, which included quartz, clay minerals, kaolinite, and iron oxides (Kaplan et al. 1994); granite and primary minerals (Torstenfelt, Rundberg, and Mitchell 1988); and humic materials (Righetto et al. 1988). Studies involving plutonium sorption recently have been reviewed by Kudo (2001) (Duff), and some main findings from this review and a few additional references will be summarized below.

Most adsorption studies have been performed with Pu(V) or Pu(VI) as initial species, because Pu(III) species is only found in anoxic systems and has received relatively less attention. Americium(III) has been studied and, though a contaminant in its own right, may serve as an analogue for Pu(III) as well. Plutonium(IV) tends to precipitate as $\text{Pu}(\text{OH})_4$ or $\text{PuO}_2 \cdot n \text{H}_2\text{O}$ or interact with suspended organic matter and is not considered available for simple surface complexation.

Geologic materials shown to strongly sorb Pu(V) include smectites and synthetic iron and manganese oxides. Zeolites, calcite, albite, quartz, and gibbsite have less affinity for Pu(V). Sorption of plutonium to smectites (Nagasaki, Tanaka, and Suzuki 1997a), manganese oxides, and calcite may be enhanced by the presence of carbonate at concentrations normally found in natural systems. Higher amounts of dissolved carbonate can inhibit sorption to iron oxides. Possibly because solution complexation competes with complexation at the Fe(III) surface.

Nelson, Orlandini, and Penrose (1989) found that freshly precipitated calcium carbonate selectively sorbed Pu(III) over Pu(IV) from solution and suggested use of this as a separation technique for analytical purposes. Given the analogy with Am(III), calcite also may effectively sorb this actinide from near-neutral solutions.

Sorption of Pu(V) to natural and synthetic geomedial can be subject to competition from other cations. Lanthanides, calcium, and magnesium all have been shown to compete for sorption sites with both Pu^{3+} and PuO_2^+ cations. Similar behavior would be expected for Am^{3+} . This is not surprising because the hard Lewis acid character of actinides, lanthanides, and alkaline earth metals, coupled with their lower charge, favors outer sphere complexation with mineral surfaces and organic matter. Thus, they are subject to ion exchange. Plutonium(IV) and Pu(VI), on the other hand, are more likely to form inner sphere complexes with surface sites because of their higher charge. This conjecture has been supported by batch studies of U(VI) and Pu(IV) sorption, but precipitation as an alternative sorption mechanism cannot be ruled out in the case of Pu(IV) (Kudo 2001 [Duff]).

Kudo (2001) (Duff) discusses a popular misconception in plutonium sorption studies that the loss of Pu(V) from solution is due to reduction to Pu(IV) species that are precipitated or strongly sorbed to geomedial. Sorption of Pu(V) to several minerals, including silica, alumina, goethite, and kaolinite, has been ascribed to this reduction process although none of these minerals can be considered significant

electron donors. Likewise, sorption of Pu(VI) to calcite was assumed to have reduced to Pu(V) upon sorption although neither Ca^{2+} nor CO_3^{2-} should serve as electron donors. Sorption to natural sediment and soil is another matter because the presence of humic materials can promote plutonium reduction as discussed above. Duff argues that spectroscopic methods such as x-ray absorption near edge structure (XANES) are required to determine true oxidation states of sorbed plutonium.

Sorption of both Am(III) and Pu(V) to alumina, silica, humic materials, and ternary complexes involving metal-humic, mineral interactions was the subject of a study by Righetto et al. (1991). Thorium(IV), which can be used as a Pu(IV) analog, and Np(V) also were included. The pHs at which 50% adsorption occurred on pure silica were 2.5 for thorium, 5.8 for americium, and 7.2 for neptunium. Plutonium(V) was studied only on alumina and resembled the sorption of Np(V). All three metals complexed with dissolved humic acid and sorption to both alumina and silica were enhanced by the addition of humic acid, which also was sorbed to inorganic phases.

Sequential extraction experiments have shown that subsurface materials have different affinities for plutonium and americium. In soil, plutonium and americium are primarily attached to organic matter and sesquioxides (Livens, Baxter, and Allen 1987; Bunzl et al. 1995; Litaor and Ibrahim 1996; Ibrahim and Moris 1997; Riekkinen and Jaakkola 2001; Loyland-Asbury, LaMont, and Clark 2001). The percentage of Pu-239 and Pu-240 associated with organic matter, determined by using sequential extraction techniques, has been reported to be more than 57% in an Alfisol under grassland (Bunzl et al. 1995) and 45–65% in Rocky Flats, Colorado, soil (Litaor and Ibrahim 1996). Although the validity of sequential extractions to determine organically bound plutonium has been questioned (Marty, Bennett, and Thullen 1997), evidence from studies that have determined plutonium activities separated by soil horizons supports that plutonium associates preferentially with organic matter. These studies have indicated that most plutonium found in soil was located in litter and organic layers (Riekkinen and Jaakkola 2001). In aquatic systems, plutonium partitioning appears to be dominated by association with organic matter (Loyland et al. 2000). Sorption of Pu(III) and Pu(IV) to aquatic sediment shows a strong inverse relation with dissolved organic carbon, with decreasing sorption to sediment, and with increasing amounts of dissolved organic carbon (UNIPUB 1982 [Wahlgren and Orlandini]), corroborating the role of organic materials either in dissolved or solid phase in sequestering plutonium.

In the few cases where the nature of the organic matter has been identified, most plutonium was associated with large molecular-weight (>150,000 Dalton) humic acid and, to a lesser degree, with fulvic acid (Livens, Baxter, and Allen 1987). Sorption mechanisms of plutonium to humic and fulvic acid are hypothesized to be complexation (Livens, Baxter, and Allen 1987).

Next to organic matter, plutonium and americium strongly associate with sesquioxides and residual fractions, such as aluminosilicate minerals (Ibrahim and Moris 1997). Sesquioxides and residual fractions sorbed 10–15% of plutonium in Rocky Flats soil (Litaor and Ibrahim 1996). Only a small portion of plutonium was associated with soluble (0.09–0.22%, shaking with distilled water) and exchangeable phases (0.04–0.08%, shaking with 0.01 molal CaCl_2 solution) (Litaor and Ibrahim 1996). In natural zeolitic tuff, Pu(V) was dominantly associated with smectites and manganese oxides rather than with iron oxides (Duff et al. 1999; Duff et al. 2001), indicating that the type of oxides influences plutonium sorption. Oxidation states of sorbed plutonium were found to be +5 and +6, which show that redox reactions can take place during sorption processes (Duff et al. 1999).

5.5.2 Microscopic Studies of Plutonium-Mineral Interactions

Several advances in analytical methods are beginning to make possible the characterization of sorbed species on geomedia, even at low concentrations, and on submicron particles (Kudo 2001 [Duff]). These microanalytical techniques include microprobe, synchrotron-based, x-ray fluorescence mapping,

which can determine the distribution of plutonium among specific phases (when used in conjunction with electron and optical microscopy techniques) and its association with other elements. Micro-x-ray absorption spectroscopy can identify the oxidation state and bonding environment (coordinating ligands, bond lengths, and coordination number) of plutonium or americium. Thus, one can determine, potentially even in natural samples, minerals to which plutonium and americium sorb, the plutonium oxidation state, and the bonding mechanism involved.

Kudo (2001) (Duff) describes application of these microanalytical techniques in laboratory studies. In one case, thin sections of Yucca Mountain tuff were exposed to synthetic groundwater containing Pu(V). Microprobe, synchrotron-based, x-ray fluorescence examination revealed that plutonium was associated primarily with smectites and manganese oxide but not with iron oxides that were also present. This occurred although equilibrium calculations suggested that Pu(V) was anionic in nature as a result of complexation with CO_3^{2-} under the solution conditions used. Mineral surfaces involved also should have been negatively-charged, which suggests that sorption occurred by means other than simple electrostatic attraction or that the stability constants for the plutonium-carbonate solution species were inadequate. Kudo (2001) (Duff) suggests that other metal cations in the solution may have caused charge reversal on mineral surfaces.

In another study XANES spectroscopy was used to determine the oxidation state of plutonium sorbed to manganese oxides. Micro-XANES uses an $\sim 10\text{-}\mu\text{m}^2$ x-ray beam to probe regions of a sample that were enriched in plutonium. By seeking out enriched areas, much lower concentrations of plutonium can be analyzed than would be expected from bulk concentrations. Plutonium(V) added to the same Yucca Mountain tuff was oxidized to Pu(VI) in the presence of smectite-rich ranceite (manganese oxide) particles. Ranceite is an Mn(IV) oxide, and Mn(IV) ions, which dominate the surface, would be expected to act as electron acceptors, reducing Mn(IV) to Mn(III) and Mn(II).

6. TRANSPORT OF PLUTONIUM AND AMERICIUM IN THE SUBSURFACE

6.1 Aqueous Solution-Phase Transport

Because of low-aqueous solubility and strong sorption of plutonium and americium, the major transport mechanisms of two radionuclides in terrestrial ecosystems generally have been considered to be erosion by water and wind, whereby plutonium and americium are translocated while attached to soil particles (Hakonson, Watters, and Hanson 1981). Transport through porous media is slow when plutonium and americium are in true solution. Long-term monitoring studies indicate transport rates for plutonium and americium through surface soil under natural conditions in the order of millimeters to a few centimeters per year (see Table 4).

Transport experiments in columns (see Table 5) show that dissolved species of plutonium and americium move slowly, except in one case where Pu(V) and Pu(VI) moved almost unretarded through powdered tuff material (see Figure 8) (Thompson 1989). Diagram (a) in Figure 8 is representative breakthrough curves for Pu(IV) and Am(III) colloids. Diagram (b) in Figure 8 is representative breakthrough curves for Pu(V) and Pu(VI). Mass recovery is indicated in parentheses in Figure 8 (based on data from Thompson 1989). Although Diagram (a) shows a representative breakthrough curve for both Pu(V) and Pu(VI), mass recovery varied considerably (between a few percent and 70%), and the cause of this variability between different breakthrough curves is not clear. Given that Pu(V) and Pu(VI) moved as fast as tritium, radionuclides likely were complexed with ligands present in effluent, which consisted of groundwater sampled from the Nevada Test Site.

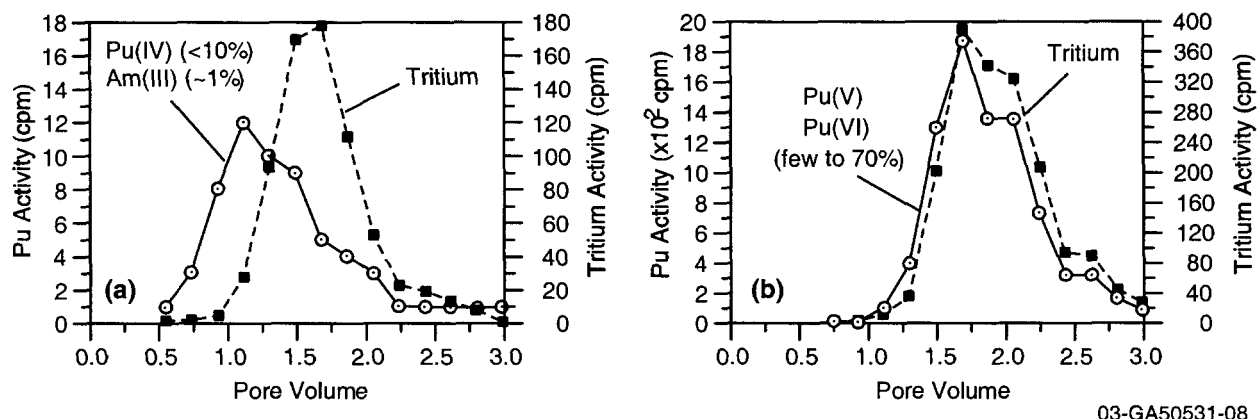


Figure 8. Breakthrough curves of tritium (dashed lines) and plutonium (solid lines) through crushed tuff from the Nevada Test Site.

In many column experiments shown in Table 5, a fast-moving fraction of plutonium and americium was observed, and this was generally attributed to colloid-facilitated transport mechanisms. As pointed out by Thompson (1989), experiments with plutonium often suffer from uncertainty about the redox reactions that can take place during the experiment and that can confound interpretation of the results.

6.2 Facilitated Transport

6.2.1 Forms of Complexes and Colloids

Significant movement of plutonium and americium in the subsurface seems possible only if plutonium and americium migration is facilitated by other compounds or materials present in the subsurface. Aqueous complexation, colloid formation, and colloid association can increase the amount of plutonium and americium in the solution phase. If these complexes and colloids are stable, fast and far-reaching transport in the subsurface can occur. Accelerated transport of radionuclides in particulate form was postulated more than 20 years ago (Apps et al. 1982; UNIPUB 1982 [Eichholz and Craft]; McCarthy and Zachara 1989). Actinides cannot only associate with naturally occurring colloidal material in the subsurface but also can form their own colloidal phases. Despite different types of classification schemes (Kim 1991), four possible forms of actinide-bearing colloids and complexes are distinguished:

- Organic colloids and organic complexes: Actinides tend to form aqueous complexes with organic material, either natural organic material, such as humic or fulvic acid, or by-products of nuclear processing or waste, such as EDTA.
- Inorganic colloids: Actinides sorb strongly to soil minerals and consequently attach strongly to natural colloidal material ubiquitously present in soil and groundwater systems, such as clay minerals and sesquioxides.
- Intrinsic actinide colloids: Actinides can form their own intrinsic colloids by polymerization. Actinides readily hydrolyze in aqueous solution, and hydrolysis is often the first step in polynucleation and polymerization of actinide ions. Intrinsic colloids are often called “true colloids” or “Eigencolloids” in literature whereas the first two types of colloids are often called “pseudocolloids.”
- Source-related, actinide-bearing colloids: Plutonium and americium are often released into the environment directly in the form of colloids. These actinide-bearing colloids stem from nuclear explosions, reactor accidents, and weathering of high-level nuclear waste glass.

These complexes and colloidal forms have different properties and will behave in distinct ways in terms of transport through the subsurface. Different forms and their implications on transport are discussed in the following sections.

6.2.2 Organic Complexes and Colloids

Organic chelating agents, either natural or present because of human activities, can increase apparent solubility of actinide ions. Complexing agents, such as NTA and EDTA, are present in waste streams containing actinides, and these organic agents cause ions like plutonium and americium to remain in the solution phase (UNIPUB 1982 [Rees and Cleveland]; Al Mahamid et al. 1996). Consequently, mobility and migration of plutonium and americium are greatly enhanced when such complexation occurs.

Both plutonium and americium are prone to complexation with organic matter. Abundant evidence shows that a fraction of plutonium and americium present in the subsurface associates with dissolved organic matter and that this association increases the effective solubility of actinides in natural systems (Cleveland and Rees 1981; UNIPUB 1982 [Rees and Cleveland]; Nelson et al. 1985; Kim et al. 1989). In the few cases where the nature of organic matter has been identified, plutonium and americium primarily associate with the larger molecular-weight fraction of dissolved organic matter, i.e., with humic acid (Alberts, Halverson, and Orlandini 1986; Agapkina et al. 1995).

Table 4. Transport rates for plutonium and americium through surface soil under natural conditions.

Location	Rainfall (mm/y)	Evaporation (mm/y)	Soil	Vegetation	Transport Rates (mm/y)			Reference
					Plutonium	Americium	Method	
Munich, Germany	800	—	Alfisol	Grassland	3–10	3–10	CM	Bunzel et al. 1994
Munich, Germany	800	—	Hapludult	Forest	0.8–7	1–20	CM	Bunzel et al. 1992
Nagasaki, Japan	2,000	800	Clay, silt, and loam	—	1.25	1.25	ADE	Mahara and Miyahara 1984; Mahara and Kudo 1995

ADE = advection-dispersion equation
CM = compartment model

Table 5. Column experiments with plutonium and americium under saturated flow conditions.

Element	Oxidation State ^a	Porous Medium	Eluent	pH	PCO ₂ (%)	Colloids	Elution Time (Pore Volume)	Reference
Pu, Am	—	Contaminated Handford sediment	GW and 0.001 molal CaCl ₂	6.2 and 8.1	0.03	In situ colloids	210	UNIPUB 1982 [Delegard, Gallagher, and Kasper]
Pu	—	Silicate sand	HNO ₃ and NH ₄ NO ₃ solutions	7.7 and 10.5	0.03	Intrinsic and organic colloids	80	Krivokhatskii, Smirnova, and Bryzgalova 1994
Pu	IV, V, VI	Crushed tuff	GW	7.1 ^b	0.03	Intrinsic colloids	3	Thompson 1989
Am	III	Crushed tuff	GW	7.1 ^b	0.03	Intrinsic colloids	3	Thompson 1989
Pu, Am	—	Crushed basalt and interbedded sediment	GW	8	0.03	Intrinsic colloids	200	Fjeld et al. 2001
Am	III	Quartz powder	0.01 molal and 0.1 molal NaCl	6.0 and 8.5	0.03	Montmorillonite	3	Nagasaki, Tanaka, and Suzuki 1997b
Am	III	Quartz powder	0–0.1 molal NaCl	6.0 and 8.5	0.03	Kaolinite	>10	Tanaka and Nagasaki 1997
Am	III	High-level waste glass	GW and 0.1–5 molal NaCl	6.0–10	0.03	Intrinsic colloids	—	Kim et al. 1985

Table 5. (continued).

Element	Oxidation State ^a	Porous Medium	Eluent	pH	PCO ₂ (%)	Colloids	Elution Time (Pore Volume)	Reference
Am	III	Aquifer quartz sand	Anerobic GW	7.6	1.0	Organic colloids	>3	Kim et al. 1994
Am	III	Aquifer quartz sand	GW	7.7–8.9	1.0	Organic colloids	15	Artinger et al. 1998
Am	III	Glauconitic sand	GW	8.4	0.03	Intrinsic colloids	—	Saltelli, Avogardo, and Bidoglio 1984
GW = simulated or sampled groundwater PCO = partial pressure of carbon dioxide a. Oxidation state of source solution b. Daniels 1982								
In all experiments listed, colloids were either present in the inflow solution or generated in situ inside the column.								

Complexation of actinides with dissolved organic molecules or humic colloids can often reduce their sorption to solid phases (UNIPUB 1982 [Wahlgren and Orlandini]). In this case, transport of plutonium and americium could be enhanced either by soluble complexes or colloid-facilitated transport. Facilitated transport by way of organic colloids has been postulated and reported for both plutonium (UNIPUB 1982 [Bondietti]; Livens, Baxter, and Allen 1987; Pavlotskay et al. 1991; Kaplan et al. 1994; Krivokhatskii, Smirnova, and Bryzgalova 1994) and americium (Kim et al. 1994; Artinger et al. 1998; McCarthy, Sanford, and Stafford 1998). Evidence for colloid-facilitated transport comes from field studies as well as from laboratory transport studies. In a field study at the Oak Ridge site, americium moved at almost the same speed as a conservative tracer through a fractured shale saprolite (McCarthy, Sanford, and Stafford 1998). Adsorption isotherms indicated that, in absence of dissolved organic matter, americium sorbed strongly to saprolite, and anion-exchange chromatography and filtration of field water samples indicated that americium was indeed complexed with dissolved organic matter (McCarthy et al. 1998; McCarthy, Sanford, and Stafford 1998). In column transport experiments, humic colloids considerably enhanced transport of americium, and colloid-bound americium moved similarly (Kim et al. 1994) or even at a slightly faster rate than average water flow velocity (Artinger et al. 1998; Artinger et al. 2002). Increased levels of humic colloids, as well as increased water flow velocity, resulted in increased mass transport of americium (Artinger et al. 1998). Interactions between humic colloids and americium were kinetically controlled (Artinger et al. 2002).

6.2.3 Inorganic Colloids

There is only scarce evidence for facilitated transport of actinides by inorganic colloids, and much of this evidence is only indirect because either direct association of actinides with inorganic colloids has not been proven, or in cases where association with colloids was demonstrated, there was no direct proof that actinide-bearing colloid really had moved through the subsurface. Based on the temporal correlation of particle concentrations and plutonium activities measured in zero-tension lysimeters, it was inferred that plutonium likely was transported through a soil profile by mobile particles (Ryan et al. 1998). Fractionation of interstitial soil water showed that plutonium and americium were associated with suspended particles larger than 0.45 μm (Litaor et al. 1998). Groundwater samples at the Savannah River site had the most plutonium associated with colloidal material larger than 500 Dalton (Kaplan et al. 1994). In most cases, the mineralogical and physicochemical nature of colloidal particles associated with actinides has not been determined. In the most comprehensive field study on colloid-facilitated transport of plutonium so far reported from the Nevada Test Site, colloidal particles were identified as native minerals occurring in the subsurface of the site, namely illite, smectite, zeolite, and cristobalite (Kersting et al. 1999). The unique setting at the Nevada Test Site allowed identification of the source of plutonium as one specific underground nuclear test (Kersting et al. 1999), which provided an accurate time mark for plutonium release. Transport velocity of plutonium was in agreement with local groundwater flow velocity, indicating unretarded movement of plutonium through the subsurface (Kersting et al. 1999). Although the possibility still exists that plutonium may have moved differently than colloid-facilitated transport (i.e., through injections through fractures), these alternatives seem unlikely at this time (Kersting et al. 1999; Honeyman 1999).

Column experiments have shown that kaolinite and montmorillonite colloids can enhance the transport of americium through quartz powder with a considerable mass transport of 70–75% within three pore volumes of the column through flow (see Figure 9) (Nagasaki, Tanaka, and Suzuki 1997b; Tanaka and Nagasaki 1997). Figure 9 is based on data from Tanaka and Nagasaki (1997) and Nagasaki, Tanaka, and Suzuki (1997b). Americium was equilibrated with kaolinite or montmorillonite colloids before injection into columns and was found to be quantitatively sorbed to the colloids (Nagasaki, Tanaka, and Suzuki 1997b; Tanaka and Nagasaki 1997); therefore, a considerable mass transport would be expected. In the absence of inorganic colloids, no americium effluent was detected within the first 10 pore volumes of column outflow.

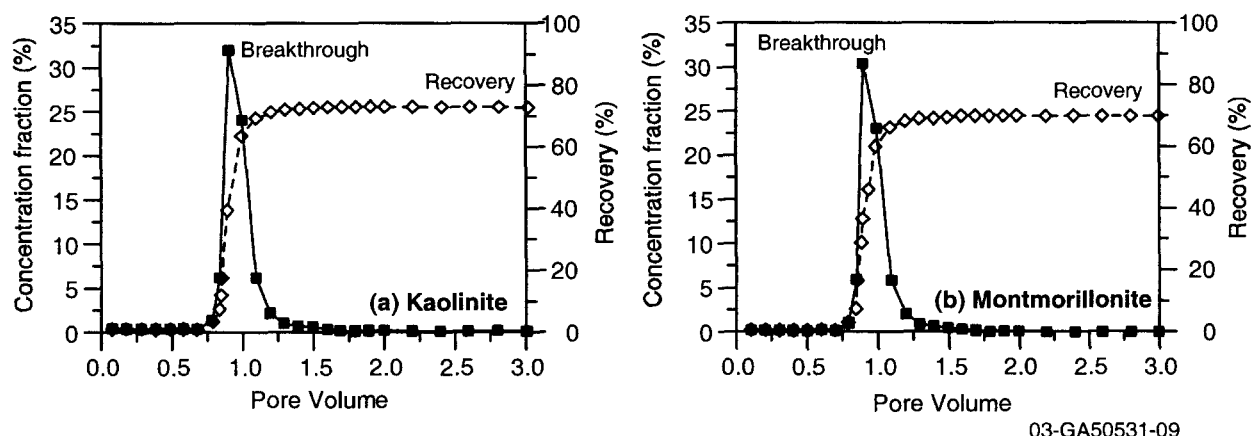


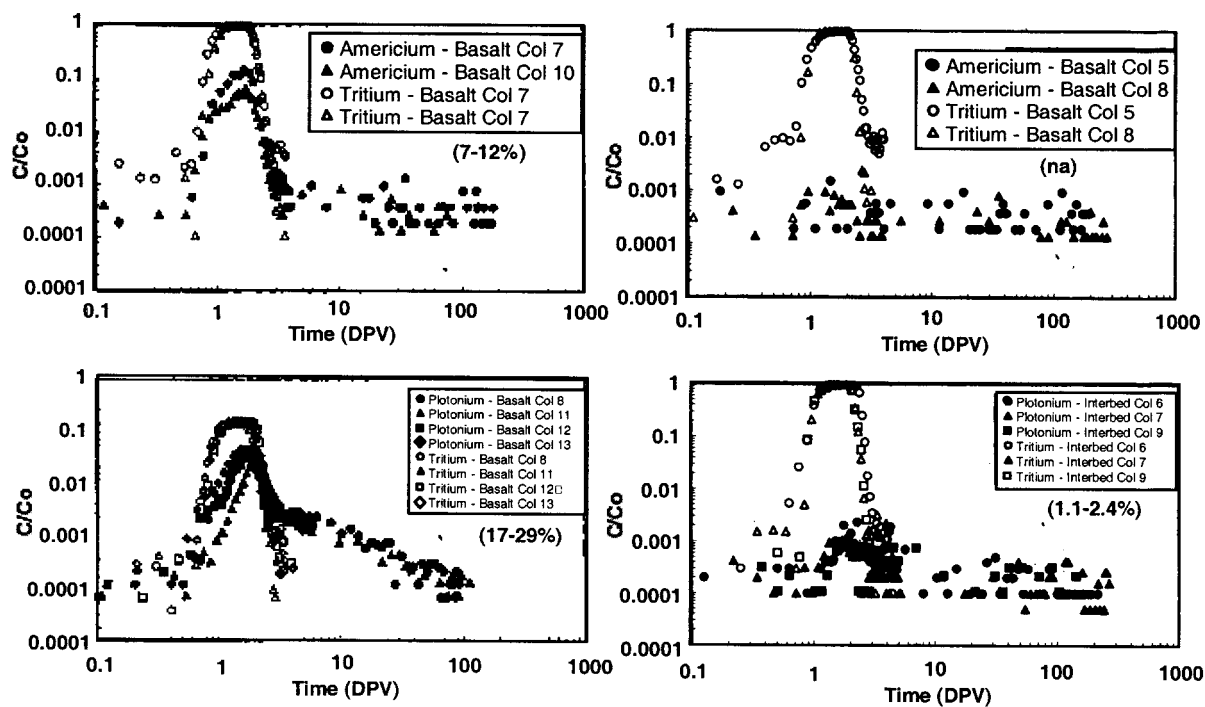
Figure 9. Transport of Americium(III) in the presence of (a) kaolinite and (b) montmorillonite colloids.

6.2.4 Intrinsic Actinide Colloids

During polymerization, colloidal particles are initially very small and will grow with time. For plutonium, particle sizes vary from <1 nm to >15 μm with increasing particle size during aging (Ichikawa and Sato 1984). It seems likely that plutonium can be transported as an intrinsic colloid. Intrinsic plutonium particles have been observed in soil at Rocky Flats (Little and Whicker 1978; McDowell and Whicker 1978); however, nothing can be inferred about migration of these particles.

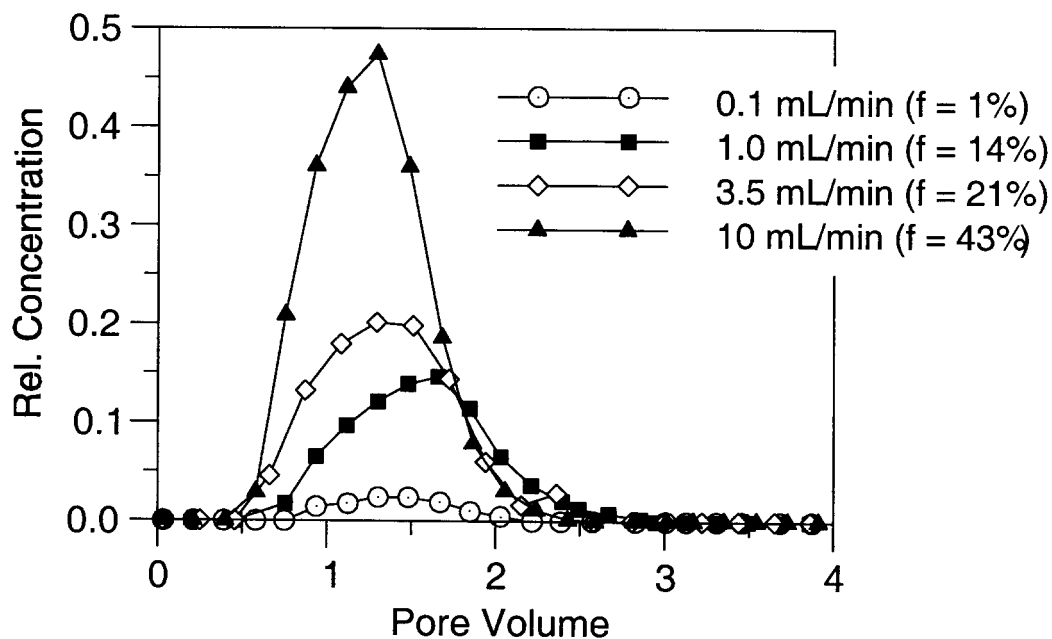
Transport of intrinsic plutonium and americium colloids has been reported from a laboratory experiment involving leaching of powdered high-level waste glass with NaCl solutions and simulated groundwater (Kim et al. 1985). Based on ultra filtration and laser-induced spectroscopy, it was determined that plutonium was leached as Pu(IV) in the form of a microcolloidal PuO_2 polymer with diameter <10 Å (Kim et al. 1985). Colloidal movement of Pu(IV) in the form of a Pu(IV) polymer also was reported from a column study with crushed tuff where a small fraction of Pu(IV) traveled faster than tritium, which was used as a conservative tracer (Figure 8a) (Thompson 1989). Similar results were obtained for Am(III) (Thompson 1989).

In column experiments with crushed basalt and basalt-interbed sediment, a fraction of plutonium and americium was transported at a fast rate and retarded less than a factor of three compared to the conservative tracer tritium (see Figure 10). In Figure 10, values in parentheses are mass recoveries in column outflow (Fjeld et al. 2001). Based on filtration experiments, this fast-moving fraction was attributed to colloidal transport (Fjeld et al. 2001) although the presence of colloids has not been proven. As the inflow solution contained a portion of plutonium and americium in colloidal form (Fjeld et al. 2001), radionuclides were likely present as intrinsic colloids. It also appears that transport of radionuclides was kinetically controlled as demonstrated by increased americium recovery in the outflow when the water flow rate increased (see Figure 11). In Figure 11, values in parentheses are mass recoveries in column outflow (Fjeld et al. 2001). Increasing bicarbonate concentrations resulted in an increase of the mass recovery of plutonium in the outflow within the first four pore volumes, indicating the presence of plutonium-carbonate complexes (Fjeld et al. 2001). Carbonate and bicarbonate are known to form complexes with plutonium and americium and actinide ions in general, and carbonate complexes can increase solubility of actinides considerably (Clark 2000). These complexes can be neutral or negatively charged (Clark 2000) and be mobile in the subsurface. Although these experiments show a fast movement of plutonium, the mechanism for this movement cannot be unequivocally determined. Either colloids or aqueous complexes are likely responsible for enhanced plutonium migration.



03-GA50531-10

Figure 10. Breakthrough curves of tritium, plutonium, and americium in crushed basalt and interbedded sediment from the Snake River Plain.



03-GA50531-11

Figure 11. Breakthrough curves of americium in crushed basalt from the Snake River Plain as a function of water flow rate.

6.2.5 Source-Related Actinide Colloids

Plutonium and americium are often released to the environment as particulates. Atmospheric bomb testing has been shown to produce actinide or actinide-containing particles with particle sizes ranging from submicrometer to centimeter scales (Crocker and O'Connor 1966; Nyhan, Miera, and Neher 1976; Cooper et al. 1993). Depending on specific conditions of the nuclear device and height of the explosion above ground, actinides can be associated with soil particles incorporated into the fireball or be highly active, spherical particles when detonation altitudes are high enough to avoid soil disturbance. Actinides released from nuclear power plants and waste storage facilities are also often associated with particles (Buck and Bates 1999; Kudo 2001 [Salbu]). Weathering of high-level waste glass has produced plutonium-bearing colloidal particles that can form stable suspensions for an extended period of time (Bates et al. 1992). During the Chernobyl reactor accident, plutonium and americium were released primarily as fuel particles with sizes ranging from a few to hundreds of micrometers (Kashparov et al. 2000). Depending on the source, relevant particle characteristics, such as size distribution, crystallographic structures, and oxidation states of actinides, will differ (Kudo 2001 [Salbu]). Fate and transport of released actinides, which depend on weathering rates and mobilization of particle-associated radionuclides, are largely source-term dependent. If released particulates are in colloidal size range, they may be dispersed in the aqueous phase and translocated through the subsurface, thereby potentially making plutonium and americium highly mobile. If, on the other hand, particulates are large inert particles, radionuclide migration through the subsurface will be delayed. Project personnel are required to know source-term characteristics to ensure an accurate assessment of plutonium and americium fate and transport (Kudo 2001 [Salbu]).

6.2.6 General Comments on Colloid-Facilitated Transport of Plutonium and Americium

Colloid-facilitated transport appears to be a likely transport mechanism for plutonium and americium. Both actinides are strongly sorbing to natural subsurface materials and will not move fast if transported only as pure soluble species. Because of their strong sorption and low solubility, plutonium and americium are ideal candidates for colloid-facilitated transport (Honeyman 1999). Attached to colloidal particles, transport velocities can be as fast as the average speed of water, and actinides can move unretarded through the subsurface, irrespective of their oxidation state. Colloid concentrations in natural subsurface systems are generally very low, limiting total mass of actinides that can be translocated by way of colloid-facilitated transport (Zhang and Brady 2002 [Honeyman and Ranville]). Direct evidence for colloid-facilitated transport of plutonium and americium is scarce. Some field studies indicate enhanced transport of plutonium by inorganic and americium by organic colloids. Clear evidence exists from laboratory column experiments that aluminosilicate and humic colloids can facilitate the transport of americium. For plutonium, such clear evidence is missing, and results are compounded by the uncertainty of the oxidation state of plutonium. Very little is known about colloidal forms of plutonium present during colloid-facilitated transport (i.e., the oxidation states of plutonium when associated with colloids) and to what extent plutonium is transported as an intrinsic, inorganically-sorbed, or organically-complexed colloid.

While in many cases colloids can facilitate movement of plutonium and americium, the claim for colloid-facilitated transport needs to be substantiated with as much evidence as possible. Sampling and measuring colloids in natural systems is not trivial. Sampling artifacts can be caused by contamination during coring, in situ mobilization of colloids during water extraction, and disturbances of the natural equilibrium between solution and solid phases during sampling. In addition, colloids and contaminants may have traveled through a different pathway than through the subsurface as illustrated in the study by Penrose et al. (1990) in Los Alamos. Penrose claimed that subsurface colloid-facilitated transport of plutonium resulted in fast migration of plutonium through the subsurface, but Penrose probably measured plutonium-bearing colloids that have entered the subsurface by way of overland flow (Marty, Bennett, and Thullen 1997).

6.3 Preferential Flow

Water flow in the vadose zone often occurs in the form of preferential flow where only a small fraction of subsurface medium is conducting flow. Preferential flow can manifest itself in various forms. In soil, preferential flow in the form of macropore flow, or unstable flow, is considered a common phenomenon (Flury et al. 1994). Preferential flow phenomena occur at different spatial scales with each scale having its distinct patterns and mechanisms (NRC 2001). Macropore flow along roots and animal burrows is obviously confined to the first few meters of soil where corresponding biological activities take place. These flow mechanisms are consequently limited to the extent of roots or animal activities. Unstable and funnel flow may extend to larger depths as they are not induced by biological activities. At even larger scales, topographic depressions or geological features, such as clastic dikes or calcic pipes and fractures, can cause large-scale water redirections and redistributions. A schematic of different forms of preferential flow phenomena in the vadose zone is shown in Figure 12 (NRC 2001). Many of these phenomena are often interconnected and can occur simultaneously.

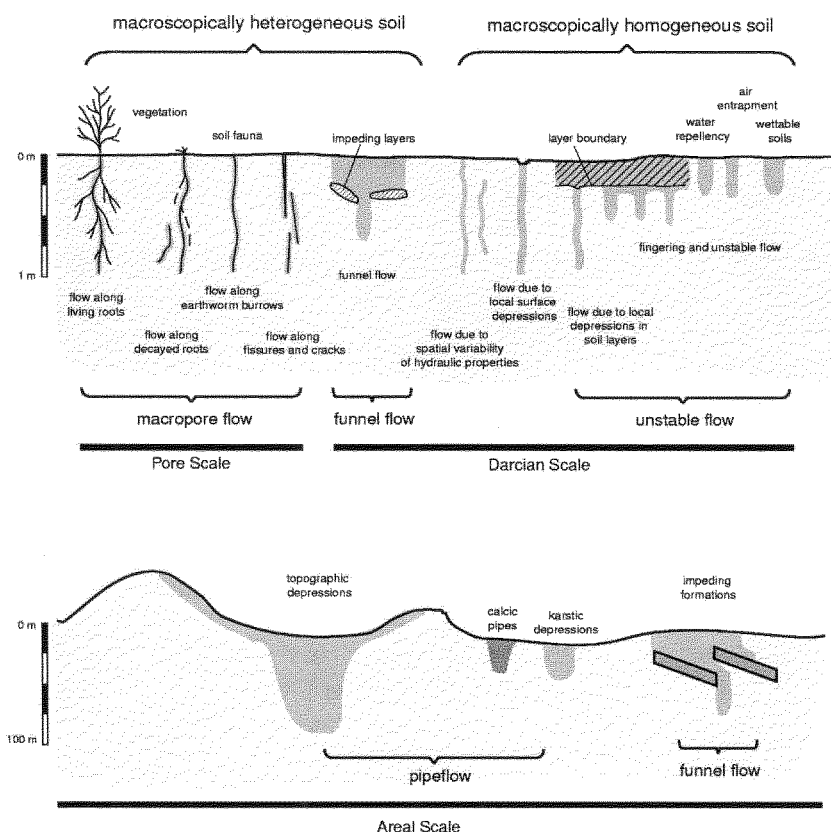
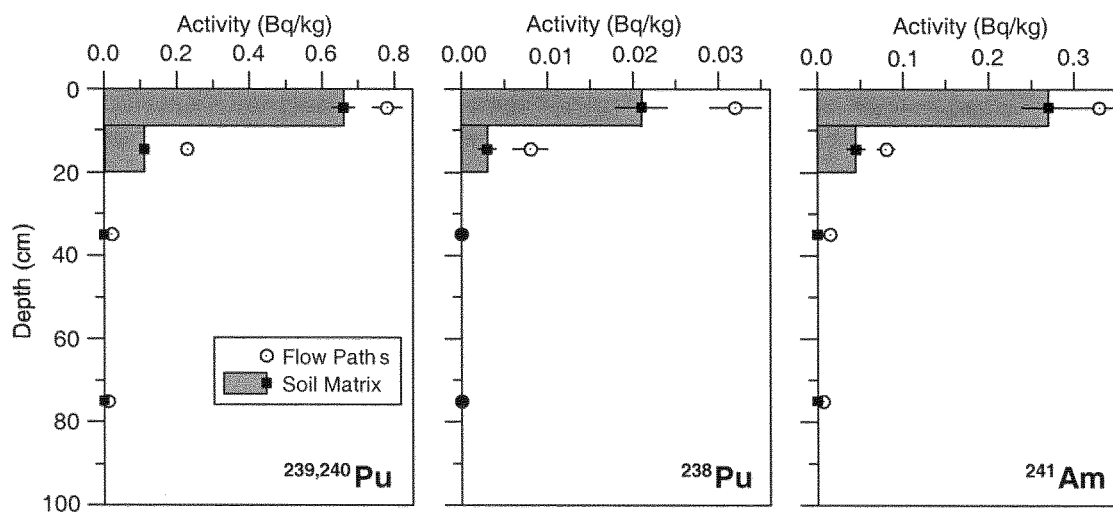


Figure 12. Schematic of different preferential flow mechanisms in the vadose zone observed at different scales.

Preferential flow has significant consequences for transport of radionuclides through the subsurface. It has been shown that in presence of preferential flow, plutonium and americium can move deeper in preferential flow channels as compared to the soil matrix (Litaor et al. 1994; Bundt et al. 2000). Bundt et al. (2000) measured plutonium and americium activities in preferential flow pathways and surrounding soil as a function of soil depth and showed that plutonium and americium indeed moved

deeper in preferential flow channels (see Figure 13). Data in Figure 13 are decay-corrected for the sampling date of March 1998. Horizontal bars represent measurement error. Figure 13 is based on data from Bundt et al. (2000). The ratio of Pu-238, Pu-240, and Am-241 in the soil samples was constant, indicating a similar migration pattern of two radionuclides. Similar results were reported for Pu-238 and Pu-240 by Litaor et al. (1994), who measured higher activities of plutonium in decayed root channels compared to surrounding soil.



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Figure 13. Depth distribution of plutonium and americium in a Cambisol under forest in Switzerland resulting from atmospheric deposition.

Whether the transport of plutonium and americium along the preferential flow path occurs as dissolved species or in colloidal form is unclear, but given the small aqueous solubility of plutonium and americium, these radionuclides, in part, likely move in colloidal or colloid-associated form through preferential flow channels (Litaor, Barth, and Zika 1996). Macropore flow can promote colloid mobilization and movement (Jacobsen et al. 1997), thereby enhancing colloidal or colloid-associated transport of plutonium and americium.

6.4 Biogenic Transport

Biological activities can translocate plutonium and americium in soil either horizontally or vertically downward and upward. Earthworms and burrowing megafauna displace large amounts of soil and consequently can translocate radionuclides sorbed to soil material. For instance, based on plutonium and americium activity distributions and analyses of earthworm casts, it was hypothesized that earthworms translocated considerable amounts of plutonium and americium from buried soil (12-cm depth) to near soil surface (3-cm depth) at Rocky Flats, Colorado (Litaor et al. 1994). Considering that enormous amounts of soil are digested by a healthy earthworm population, i.e., up to 50,000–1,000,000 kg soil per year hectare (Brady and Weil 2001), this transport and mixing mechanism is important to consider when earthworms are present. Obviously, translocation of radionuclides in soil by organisms is confined to the organisms' habitats. In the case of earthworms, some species can burrow to 6 m deep, but, in general, activities are confined to the top 2 m (Miller and Gardiner 2001).

Actinides can sorb to microbial surfaces, can be assimilated and absorbed in living cells, and can be complexed by microbial exudates (Wildung and Garland 1977; Mahara and Kudo 1998; Kudo 2001

[Mahara and Kudo]). Furthermore, microorganisms can induce local changes of pH and redox potentials, thereby affecting solubility and mobility of actinides (Kudo 2001 [Francis]). Reduction potential of hydrous PuO_2 is similar to that of $\alpha\text{-FeOOH}$, and it seems likely that iron-reducing bacteria also can reduce Pu(IV) to Pu(III), thereby considerably increasing plutonium solubility (PuO_2 : $\log K = -63.3$; $\text{Pu}(\text{OH})_3$: $\log K = -24$) (Kudo 2001 [Francis]). Organic acids, extracellular metabolites, and siderophores also will increase plutonium solubility while biosorption and bioprecipitation reactions will lead to plutonium immobilization (Kudo 2001 [Francis]). Siderophores can complex Pu(IV), and the plutonium-siderophore complex can be taken up by microorganisms although plutonium uptake through this mechanism is much slower and less than iron uptake (John et al. 2001). Adsorbed and absorbed actinides can be translocated together with moving microorganisms (e.g., bacteria). The quantitative magnitude of microbial-facilitated transport depends on amount of sorption, type of exudates, and ability of microorganisms to move through the subsurface.

6.5 Vadose Zone Transport Versus Groundwater Transport

The physics of water flow in the vadose zone and groundwater are fundamentally different. In addition, geochemical conditions, such as redox potential, pH, and ionic strength, are different in the vadose zone and groundwater. Consequently, fate and transport of plutonium and americium also will differ fundamentally between the two subsurface systems. The following list summarizes major unique characteristics of the vadose zone relevant for fate and transport:

- Unsaturated and saturated flow obeys different physical laws for flow
- Episodic events, such as rainfall events, preferential flow phenomena, or snowmelt, may dominate movement of contaminants in the vadose zone
- Air-liquid interface may provide sorption or temporary attachment sites for colloidal particles
- Organic matter content is usually highest in the topsoil and decreases with increasing soil depth
- Organic and inorganic colloidal material can be mobilized during rainfall events, and soil-forming processes continuously generate colloidal material
- Redox conditions can vary temporally but are generally characterized by oxidizing conditions unlike in groundwater where redox conditions are more stable.

7. CONCEPTUAL MODEL FOR PLUTONIUM AND AMERICIUM FATE AND TRANSPORT

7.1 General Conceptual Model

A conceptual model for plutonium reaction processes in the vadose zone is depicted in Figure 14. Arrows in Figure 14 indicate the direction of reactions. The model contains major geochemical reactions that plutonium can undergo, including hydrolysis, complexation, polymerization, precipitation, sorption, and colloid attachment and detachment to interfaces. Plutonium can occur in all four oxidation states simultaneously, yet, one oxidation state will usually dominate the aqueous system depending on pH and Eh conditions. The model depicted shows the complexity involved when dealing with an element like plutonium. For constant geochemical conditions, the model can be considerably simplified because certain processes will become less relevant than others. However, as geochemical conditions change temporally, in particular in the vadose zone, as well as spatially during migration of plutonium through the subsurface, major simplifications are unlikely adequate. A reliable plutonium fate and transport model applicable to field conditions likely will have to include all major processes shown in Figure 14 with minor modifications for major oxidation states of plutonium in the local environment. Such a conceptual model could be best implemented in a two-phase reactive transport model.

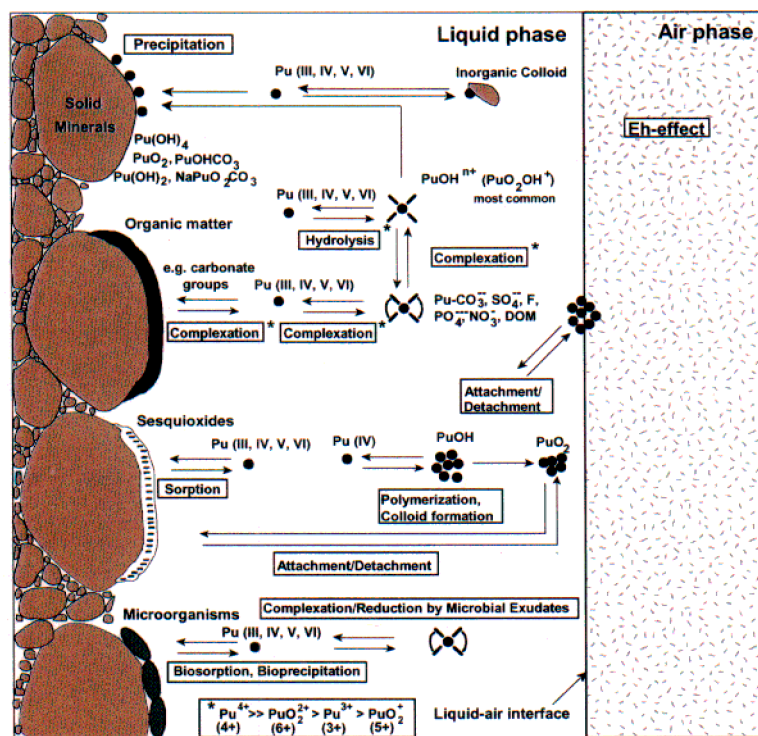


Figure 14. Conceptual model of plutonium reaction processes in an unsaturated subsurface system.

The conceptual model for americium is very similar to that of plutonium except that no redox reactions are present (see Figure 15). Arrows in Figure 15 indicate the direction of reactions. The geochemistry of americium is nevertheless complex, involving hydrolysis, complexation, precipitation, sorption, colloid formation, and microbial interactions. Like for plutonium, aqueous-phase concentrations of americium likely are to be dominated by complexed or colloidal-phase americium. Transport of both actinides in the subsurface likely is governed by colloidal transport mechanisms.

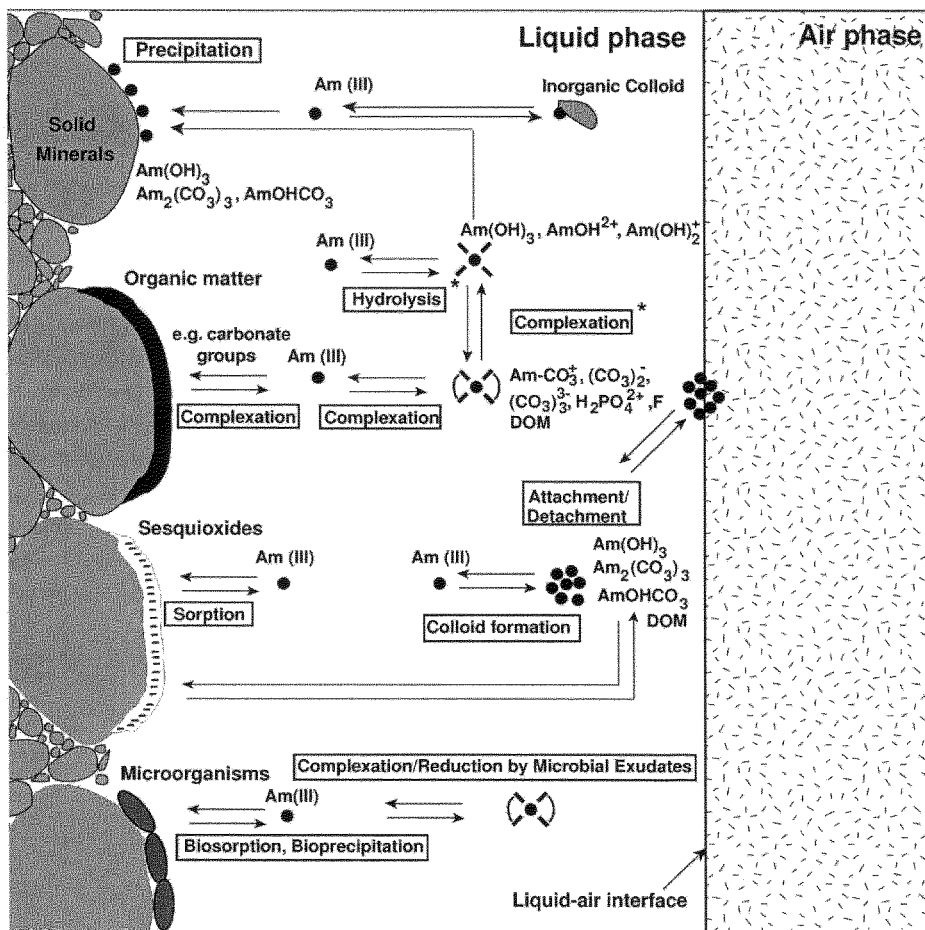


Figure 15. Conceptual model of americium reaction processes in an unsaturated subsurface system.

7.2 Colloid Transport Mechanisms

Transport of colloids, whether organic or inorganic, is governed by attachment and detachment processes, which are generally described by filtration theory. Filtration theory often describes colloid-solid phase interactions as an irreversible process, leading to a macroscopically first-order removal of colloidal particles from the aqueous phase. The first-order process is valid when unlimited attachment is possible; in the case of site blocking, reaction kinetics become more complicated, and different approaches of site blocking have been proposed in literature (Kretzschmar et al. 1999; Ko and Elimelech 2000). In most cases, researchers assume that attached colloids do not subsequently detach although slow detachment kinetics have been observed for certain colloidal materials. Governed by the balance between attractive (van der Waals) and repulsive (electrostatic) forces (DLVO theory^a), colloids can move with the velocity of water, can move faster than the average velocity of water because of pore-size exclusion effects, or can be filtered out completely during transport. Filtration efficiency is determined by pore-size distribution, surface charges, ionic strength, and steric effects.

a. This theory is named after the individuals who developed it—Derjaguin, Landau, Verwey, and Overbeek.

Besides solid-liquid (attachment and detachment) and solid-solid (aggregation and coagulation) interactions, colloidal particles also can associate with the liquid-gas interface in a porous medium. Attachment to liquid-gas interfaces will cause additional removal of colloidal material from the mobile liquid phase; however, removal might be only temporary because the liquid-gas interface is dynamic and can decrease or increase in area, depending on the water content in the vadose zone. A stationary liquid-gas interface tends to retain colloidal particles through capillary forces (Wan and Wilson 1994; Wan, Wilson, and Kieft 1994) or through film straining (Wan and Tokunaga 1997). The latter mechanisms become effective when water content falls below a critical threshold such that water films become smaller than the diameter of colloidal particles (Wan and Tokunaga 1997). Gas bubbles themselves can be mobilized and move with water flow, thereby carrying along colloids attached at the liquid-gas interface (Wan and Wilson 1994).

A simple colloid filtration model is shown in Figure 16. Arrows in Figure 16 indicate first- or higher-order reactions. The model shows solid-liquid and liquid-gas phase interactions of colloidal particles, and the arrows indicate first- or higher-order reactions. Most commonly, first-order interactions have been assumed.

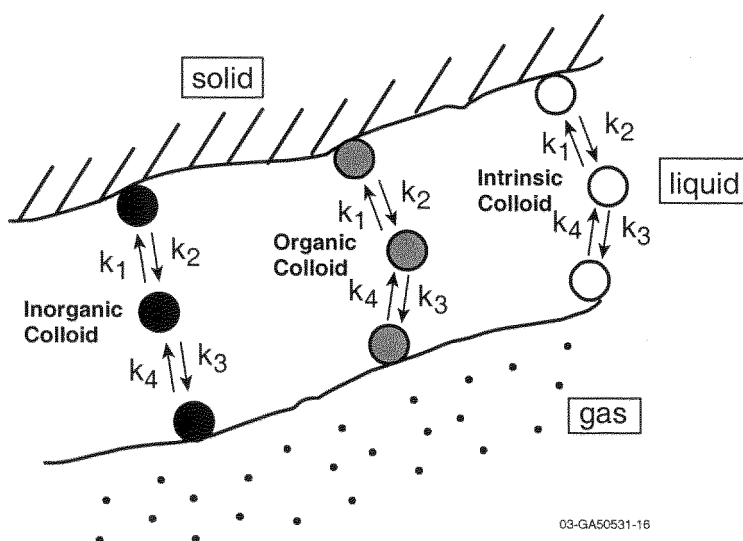


Figure 16. Conceptual model of colloid interactions with solid-liquid and liquid-gas interfaces.

Several recent review articles discuss colloid transport mechanisms for both inorganic (Ryan and Elimelech 1996; Kretzschmar et al. 1999) and organic (Schijven and Hassanizadeh 2000; Jin and Flury 2002) colloids.

7.3 Models Based on Distribution Coefficients

Given the complexity of plutonium geochemistry, a model based on distribution coefficients alone is likely to fail to predict plutonium fate and transport accurately. Not only will changes in solution chemistry and associated changes in oxidation states not be represented adequately, but also kinetically controlled processes such as colloid formation, filtration, or precipitation cannot be considered appropriately (McKinley and Alexander 1992).

Models based on distribution coefficients, however, may be useful for sensitivity analysis or to assess the relevance of certain processes on overall mass transport. An example of such an approach is

demonstrated by Vilks, Caron, and Haas (1998) and Contardi, Turner, and Ahn (2001), who used the linear sorption concept to estimate the relative magnitude of colloid-facilitated transport for risk assessment purposes. In this approach, retardation of a contaminant based on linear equilibrium sorption with distribution coefficient K_d^b (see Equation [7]) is modified to include colloid-facilitated transport (see Equation [8]).

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad (7)$$

$$R_{eff} = 1 + \frac{1}{1 + CFK_d} \frac{\rho_b}{\theta} K_d \quad (8)$$

where

ρ_b = bulk density (mass of dry soil per total volume of soil)

θ = volumetric water content

C = colloid concentration

F = an empirical factor such that $K_{d,colloid} = FK_{d,porous\ medium}$.

Factor F can be related to specific surface areas (A) of colloids and porous medium in Equation (9), which weighs the increased sorptive capacity of colloidal material according to increased surface area (Contardi, Turner, and Ahn 2001).

$$F = A_{colloid} / A_{porous\ medium} \quad (9)$$

Such a model has been used to estimate the effect of colloid concentrations on long-term radionuclide mobility (Contardi, Turner, and Ahn 2001).

A refinement of the equilibrium distribution approach would be to incorporate colloid filtration into the existing transport model. A conceptual colloid filtration model for an unsaturated porous medium, including three types of actinide colloids: inorganic, organic, and intrinsic, is shown in Figure 16. The conceptual model accounts for kinetic attachment and detachment of colloidal particles to both liquid-solid and liquid-gas interfaces. Attachment and detachment reactions can be represented with different types of kinetics, such as first- or higher-order reactions, incorporating site blocking as described in review articles (Jin and Flury 2002).

7.4 Parameterization of Conceptual Models

Complete conceptual models for plutonium and americium transport include both geochemical and colloidal transport processes. Geochemical reactions are complicated, but most of the solution-phase

b. The equations here are written in the more general form with the volumetric water content θ in lieu of the porosity to extend the analysis to unsaturated porous media.

equilibrium constants have been identified (see Table 3) so that a geochemical model will be able to describe plutonium and americium species. However, some equilibrium constants are still questionable and must be verified.

Interactions of the colloid with the solid-liquid interface and the liquid-gas interface are difficult to parameterize because these reactions will depend on the type of colloids (composition in terms of mineralogy or organic matter) and because reactions seem to be dependent on water content of the porous medium. An a priori determination of these attachment and detachment processes has not been made for field conditions but so far only for controlled laboratory experiments. A posteriori calibration of attachment and detachment processes, however, has been successfully executed for colloidal transport in groundwater systems but not in the vadose zone. Given that colloidal processes are likely the dominant mechanisms for far-reaching and fast plutonium and americium transport, more information regarding colloid attachment and detachment in the vadose zone is needed.

The colloid-facilitated transport model based on distribution coefficients is relatively easy to parameterize; parameters involved are sorption coefficient (K_d), bulk density (ρ_b), water content (θ), ratio of specific surface areas of colloids and porous media (F), and colloid concentration (C).

A colloid filtration model (see Figure 16) requires parameterization of the liquid-solid interfacial reactions of actinide-bearing colloids. The type of these reactions and parameterization possibly could be determined based on column breakthrough experiments.

8. FUTURE WORK TO REDUCE UNCERTAINTIES IN PLUTONIUM AND AMERICIUM MIGRATION PREDICTIONS AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY

The conceptual models for plutonium and americium fate and transport developed in the previous section are formulated in the most general way. As such, they incorporate all relevant processes potentially occurring in the subsurface. At specific waste sites, geochemical and hydrological conditions may be such that certain processes dominate over others, and consequently, general conceptual models can be simplified. The simplification of conceptual models requires synthesis and incorporation of site-specific information to assess which processes can reasonably be neglected. In addition, the site-specific source of plutonium and americium contamination is an important factor to consider as plutonium and americium may be released in specific chemical forms to the subsurface or may be present in specific, unique waste streams.

For the Idaho National Engineering and Environmental Laboratory (INEEL) Subsurface Disposal Area (SDA), site-specific information needed to develop an adequate, simplified conceptual model seems to be available (Holdren et al. 2002; Magnuson and Sondrup 1998; Becker et al. 1998; Ibrahim and Moris 1997). Site-specific plutonium distribution in different soil phases near the SDA has shown that, in surface soil, plutonium is mainly associated with carbonates, organic material, sesquioxides, and silicates (Ibrahim and Moris 1997). Only a small fraction of plutonium was associated with soluble and exchangeable sites (Ibrahim and Moris 1997). Based on this information, it seems likely that the major transport mechanism for plutonium will be colloidal. However, presence of colloids first must be experimentally confirmed.

A conceptual model for flow and transport at the Radioactive Waste Management Complex has been developed and implemented (Magnuson and Sondrup 1998). The model has been shown to describe hydrology of the site reasonably well, but radionuclide transport does not seem to be represented well. The conceptual model of Magnuson and Sondrup (1998) assumes that radionuclides sorb with a linear and equilibrium process, and colloid-facilitated transport is not considered. A very general conceptual model for plutonium and americium fate and transport has been discussed in this review. For the SDA, a more specific conceptual model (i.e., a simplified version of the general model) can and should be deduced. A model based on linear equilibrium sorption (K_d approach) is not likely to provide an accurate prediction of plutonium and americium fate and transport at the INEEL site. Geochemical and hydrological conditions in the SDA subsurface are too variable and heterogeneous so that a geochemical model in combination with colloidal transport mechanisms should be combined with the already-existing hydrological model.

Specific issues related to the SDA, and to be included in the conceptual model, are discussed in the following sections.

8.1 Occurrence and Distribution of Plutonium and Americium in the Idaho National Engineering and Environmental Laboratory Vadose Zone

Plutonium has been detected, although only sporadically, in the vadose zone and the groundwater (Holdren et al. 2002). Based on monitoring data, plutonium was suggested to be present not as a continuous plume but as randomly occurring particles (Holdren et al. 2002). This observation, together with the fact that plutonium was detected at depths of >42 m (140 ft), indicates a colloidal transport mechanism, preferential flow, or a combination of the two.

Americium has been observed together with plutonium in the vadose zone (Holdren et al. 2002). Other data, however, do not show a strong correlation between americium and plutonium detections. Although americium and plutonium likely have similar transport mechanisms, available data do not consistently support this hypothesis.

While reported data indicate a sporadic temporal and spatial occurrence of plutonium and americium, radionuclides clearly have moved much deeper than expected based on aqueous solution transport. It seems that colloidal transport is occurring, but no hard evidence is available to date. Constructing depth profiles of radionuclide distributions (and also of other chemicals available) from reported data (cores and lysimeters) would be helpful; it may provide a better picture of trends and patterns of radionuclide distribution.

8.2 Hydrology and Hydrogeology

Hydrology and hydrogeology at the INEEL site are very complex because of the interplay between fractured basalt and sedimentary interbeds. Water flow in the vadose zone likely is influenced to a large degree by preferential flow. Episodic events during snowmelt and rainfall cause transient conditions and may trigger preferential flow. Sedimentary interbeds overlaying basalt rock can cause perched water tables to form, which in turn can trigger preferential or fractured flow through basalt. In regard to plutonium and americium transport, hydrological conditions have several implications: (1) rapid flow through fractures can reduce contaminant sorption by reducing the effective surface area available for sorption as well as by reducing time available for equilibrium sorption to occur; (2) perched water tables imply a change in redox conditions, which is very relevant for plutonium speciation; (3) the vadose zone is stratified and mineralogically and chemically heterogeneous, resulting in different geochemical conditions in different depths; and (4) it has been reported that most fractures have clay liners (Holdren et al. 2002), indicating that colloidal transport is frequent and naturally occurring. Colloid-facilitated transport of plutonium and americium are likely to occur as well.

A geochemical transport model requires spatially distributed geochemical and hydrological data that do not seem to be available at the INEEL site. Geochemical and hydrological properties as a function of depth should be assessed for the vadose zone below the SDA.

8.3 Chlorinated Solvents

Existence of mixed waste (INEEL 2000), containing metals, radionuclides, and organic solvents, presents a difficult remediation problem. Techniques that would normally be used to clean up one type of contaminant, in many cases, will not affect other contaminants. In other cases, it may create new problems for one or more of the other contaminants. For example, chlorinated hydrocarbons, such as carbon tetrachloride and trichloroethylene, may be removed from subsurface materials by volatilization. Vacuum enhanced thermal desorption is an example of such a process and could be used in the presence of plutonium and americium, but radionuclides would not volatilize. This would leave waste that is only partially remediated but still may constitute an improvement over mixed waste. In such a case, an examination of any changes of the state of plutonium and americium as a result of thermal treatment should be considered. Another common treatment of chlorinated hydrocarbons involves the use of reactive barriers designed for reductive decomposition of compounds. Metallic iron can be used for this purpose, but the affect on accompanying plutonium and americium is unknown. Reduced plutonium would be more soluble than Pu(IV) so such a transformation could be undesirable. Americium(III) and Pu(III), on the other hand, might substitute for Fe(III) in $\text{Fe}(\text{OH})_3$ products of iron metal oxidation. Given that Am(III) has a larger ionic radius than Fe(III), one would expect substitution to be limited. In short, the mixed waste problem will require solutions that consider side reactions of accompanying solutes, colloidal materials, and solvents. It is unlikely that a method developed for one waste can effectively treat

mixed waste without modification and, in some cases, could result in a more reactive form of the untreated contaminant.

8.4 Complexing Agents

Both inorganic and organic complexing agents may be present.

8.4.1 Inorganic Complexes

Plutonium and americium are present in the SDA in combination with high-nitrate concentrations. Nitrate is a complexing agent for both plutonium and americium and can increase aqueous solubility of radionuclides, rendering them more mobile in the subsurface. Also, carbonate can form complexes. For plutonium, nitrate and carbonate complexes are not likely too important because aqueous species will be dominated by hydrolysis. For americium, on the other hand, carbonate complexes are likely to play an important role in increasing americium solubility. Fluoride and phosphate are also strong complexing agents. Measuring nitrate, carbonate, phosphate, and fluoride concentrations in pore water and groundwater would be useful.

8.4.2 Organic Complexes

Organic complexing agents, such as EDTA, diaminocyclohexane tetraacetic acid, and citric acid, are present in Rocky Flat waste streams (INEEL 2000). These chemicals are very strong complexing agents, particularly EDTA, and plutonium and americium complexes likely exist at INEEL. In addition, natural organic materials, in particular humic acid, also contribute to actinide complexation.

Laboratory batch and column experiments using INEEL-site basalt and interbed sediment have shown that americium and Pu(IV) sorption is considerably reduced in the presence of EDTA; no effect was observed for Pu(V).

Information is needed about the presence of these complexing agents (EDTA, diaminocyclohexane tetraacetic acid, citric acid, and humic acid) in pore water of the vadose zone of the Radioactive Waste Management Complex. Although not a proof for enhanced actinide transport, the presence of these complexing agents in cores and lysimeters would point to a potentially important transport mechanism.

8.5 Waste Streams

Plutonium at the SDA is contained in a variety of different waste streams, including wasted laboratory equipment, ash, organic sludge, and inorganic sludge (Becker et al. 1998; Holdren et al. 2002). Plutonium can be released from these sources either in aqueous, dissolved form or as particulates. Depending on the source and form of the release, the oxidation state of plutonium likely will differ as well, thereby influencing the environmental behavior of the actinide. Analysis of fluids from the waste deposits would reveal in which form plutonium and americium are released from the waste.

8.6 Effect of Sampling Techniques on Assessment of Plutonium and Americium Fate and Transport

The nature and extent of contamination in the subsurface at the INEEL site are monitored by different methods, such as suction lysimeters, core sampling, and groundwater sampling from wells. All these methods have advantages and disadvantages and can cause sampling artifacts. Very little information is available at present on the effect of these sampling methods to determine colloid concentrations. Groundwater sampling and cores are suspected to yield higher-than-natural colloid concentrations because of disturbances of local water flow field or physical disturbance of the porous

medium itself. Suction lysimeters will suffer from a similar artifact during installation but usually will operate under low fluxes after installation so that local colloid mobilization seems unlikely. However, dissolved radionuclides may sorb, and suspended colloids may stick to the walls of ceramic porous cups, which has been supported both by laboratory experimentation as well as field sampling showing generally smaller americium concentrations in suction lysimeters compared to core samples (Holdren et al. 2002). Stainless steel porous cups might reduce sorption of aqueous species but will not necessarily be inert for colloid sampling. At the INEEL, personnel have observed that stainless steel membranes tend to filter out colloidal material although pore sizes of the membranes were much larger than the colloid sizes. Systematic tests in this regard do not exist or are not known at this time. Many different types of porous material are available, ranging from Teflon and porous plastic to stainless steel and ceramic, and systematic tests regarding sampling of colloidal particles would be highly valuable.

Data on plutonium and americium from suction lysimeters at Radioactive Waste Management Complex have shown sporadic occurrence of the two radionuclides, but no clear trends have been detected on whether a widespread contamination or a migrating contaminant plume is present (Holdren et al. 2002). Higher detection frequencies for americium were found in soil cores compared to suction lysimeters (Holdren et al. 2002), indicating possible retention of americium in porous cups. Systematic experimental studies should be conducted to determine the representativeness of suction devices in regard to sampling pore water for americium, plutonium, and colloidal particles.

8.7 Colloid Concentrations and Composition in Pore Water and Groundwater

If colloid-facilitated transport occurs, colloidal material could be measured in the pore water. Colloids can come in different sizes, ranging from nonfilterable humic acid to m-sized inorganic colloids. Intrinsic colloids can vary over a large magnitude of sizes. Pore water should be analyzed for the presence of colloidal material. While this is possible, although difficult, in the saturated zone, colloid sampling in the unsaturated zone is challenging. Zero-tension lysimeters have been employed in some cases, but suction lysimeters must first be shown to produce reliable results. Through such measurements, not only would the presence of colloids be verified, the simple conceptual model based on the distribution coefficient also requires knowledge on type (surface area) and concentrations of colloids.

8.8 Filtration and Dialysis of Pore and Groundwater Samples

Samples taken from lysimeters and wells could be filtered sequentially with different filter sizes and dialysis membranes to determine whether colloidal plutonium and americium are present. Also, the presence of nonfilterable anionic plutonium and americium complexes in the pore and groundwater could be analyzed with an ion-exchange membrane or ion-exchange column.

8.9 Modeling Analysis of Column Breakthrough Experiments from Fjeld's Article

The experimental data set of Fjeld's article, "Characterization of the Mobilities of Selected Actinides and Fission/Activation Products in Laboratory Columns Containing Subsurface Material from the Snake River Plain," (Fjeld et al. 2001) could be analyzed with mechanistic models to elucidate exact mechanisms and processes responsible for the observed fast transport of a small fraction of actinides. This analysis also would yield quantitative parameters for a colloid filtration model as shown in Figure 16.

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